I ndian Vol. The characteristic of square complexes \([\text{VO(\text{Bptbh})]}\) and \([\text{Fe(\text{HBptbh})(acac)}]\) has been found to form complexes. magnetic susceptibility measurement, UV-vis, IR, ESR, \(^1\)H NMR. ESR spectra of \(\text{Mbs Bauer}\) and FAB mass spectral studies. The room temperature ESR spectra of \(\text{OV}^{\text{IV}}, \text{Fe}^{\text{II}}\) and \(\text{Cu}^{\text{II}}\) complexes yield \(g\) values characteristic of square pyramidal, octahedral and square planar complexes, respectively. The Mössbauer spectra of \([\text{Fe(\text{HBptbh})(acac)}]\) at room temperature and 78 K suggest the presence of high spin \(\text{Fe}^{\text{II}}\). The solid state conductivity of \([\text{VO(\text{Bptbh})]}\), \([\text{Fe(\text{HBptbh})(acac)}]\) and \([\text{Cd(\text{HBptbh})]}\), increase in temperature range 323-333 K with a band gap of 0.42-0.75 eV, indicating their semiconducting behaviour. Other complexes are insulators.

Over the last more than one decade, there has been a dramatic growth of interest in inorganic complexes based materials that exhibit unusual solid-state properties. Some sulphur and nitrogen containing ligands and their complexes have been found to be important precursor for semiconducting materials\(^1\) used as photosensitizer for conversion of light energy to electricity. Some work has been reported on 3d metal complexes of \(p\)-hydroxythiobenzhydrazide\(^3\) and its N-aryl derivatives\(^5\). In view of this, we synthesized N-benzoyl-N'\(\text{-}\)p-hydroxythiobenzhydrazine (Structure I) having oxygen, nitrogen and sulphur donors and studied their structure and solid state electrical conductivity.

**Synthesis, characterization and electrical conductivities of some transition metal complexes of N-benzoyl-N'\(\text{-}\)p-hydroxythiobenzhydrazine**

N K Singh* & S K Kushawaha
Department of Chemistry, Banaras Hindu University, Varanasi 221 005, India

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A new potential tetradentate ligand, N-benzoyl-N'\(\text{-}\)p-hydroxythiobenzhydrazine (\(\text{H}_2\text{Bptbh}\)) has been found to form complexes \([\text{VO(\text{Bptbh})]}\), \([\text{Fe(\text{HBptbh})(acac)}]\) and \([\text{M(\text{HBptbh})]}\) (\(\text{M} = \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}\)) by loss of one or two proton(s) from the ligand. The complexes have been characterized by elemental analyses, magnetic susceptibility measurement, UV-vis, IR, ESR, \(^1\)H NMR, Mössbauer and FAB mass spectral studies. The room temperature ESR spectra of \(\text{OV}^{\text{IV}}, \text{Fe}^{\text{II}}\) and \(\text{Cu}^{\text{II}}\) complexes yield \(g\) values characteristic of square pyramidal, octahedral and square planar complexes, respectively. The Mössbauer spectra of \([\text{Fe(\text{HBptbh})(acac)}]\) at room temperature and 78 K suggest the presence of high spin \(\text{Fe}^{\text{II}}\). The solid state conductivity of \([\text{VO(\text{Bptbh})]}\), \([\text{Fe(\text{HBptbh})(acac)}]\) and \([\text{Cd(\text{HBptbh})]}\), increase in temperature range 323-333 K with a band gap of 0.42-0.75 eV, indicating their semiconducting behaviour. Other complexes are insulators.

**Experimental**

All chemicals used were of analytical reagent or equivalent grade. Benzoic acid hydrazide\(^6\), ammonium polysulphide\(^7\) and carboxymethyl-p-hydroxydithiobenzoate\(^8\) were prepared by literature methods. Bis(acetylacetonato) oxovanadium(IV) and tris(acetylacetonato) iron(III) were prepared by reported procedures\(^9\).

**Preparation of \(\text{H}_2\text{Bptbh}\)**

N-Benzoyl-N'\(\text{-}\)p-hydroxythiobenzhydrazine (\(\text{H}_2\text{Bptbh}\)) was prepared by reacting solutions of benzoic acid hydrazide (2.72 g, 20 mmol) and carboxymethyl-p-hydroxydithiobenzolate (4.0 g, 20 mmol) each dissolved separately in 40 mL of 0.5 \(N\) NaOH solution followed by dropwise addition of dilute acetic acid (20%) to the above reaction mixture, after letting the solution stand for 2 h. The product which precipitated was filtered, washed with water and recrystallized from hot ethanol, mpt \(126^\circ C\), yield \(80\%\).

**Preparation of the complexes**

\([\text{M(\text{HBptbh})]}]\)

The complexes of the type \([\text{M(\text{HBptbh})]}\) (\(\text{M} = \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}\)) were prepared by refluxing together methylnol/ethanolic solutions (30 mL) each of \([\text{M(\text{OAc})}_2\text{H}_2\text{O}]\) (1 mmol) and \(\text{H}_2\text{Bptbh}\) (0.54 g, 2 mmol) for 1 h. The solid complexes obtained were filtered, washed with ethanol and dried in \textit{vacuo}.

\([\text{VO(\text{Bptbh})]}\) and \([\text{Fe(\text{HBptbh})(acac)}]\)

\([\text{VO(\text{Bptbh})]}\) and \([\text{Fe(\text{HBptbh})(acac)}]\) were prepared by refluxing methylnolic solutions (25 mL) each of \([\text{VO(acac)}]_2\) (0.26 g, 1 mmol) or \([\text{Fe(acac)}]_3\) (0.35, 1 mmol) and \(\text{H}_2\text{Bptbh}\) (0.27 g, 1 mmol or 0.54 g, 2 mmol) for \(ca\) 3 h. The precipitated complexes were suction filtered. The oxovanadium(IV) complex was washed with \(\text{CHCl}_3\), while \([\text{Fe(\text{HBptbh})(acac)}]\) was washed with methanol and dried in \textit{vacuo}.

Methods of analyses and techniques employed for the physico-chemical measurements were the same as described elsewhere\(^9\).

**Results and discussion**

\([\text{M(\text{HBptbh})]}\) (\(\text{M} = \text{Cu}^{\text{II}}, \text{Zn}^{\text{II}}, \text{Cd}^{\text{II}}\)), and \([\text{Fe(\text{HBptbh})(acac)}]\) were formed by loss of one
proton from each ligand while [VO(Bptbh)] was formed by loss of two protons from the ligand (Table I). All the complexes were found to be insoluble in water, ethanol, methanol, chloroform and acetone. [Zn(HBptbh)₂] was found to be soluble in polar organic solvents such as DMSO and DMF and melts at 145°C. Because of steric considerations, all the four potential sites in [VO(Bptbh)] cannot be attached to a single metal and, therefore, the ligand binds in a polymeric fashion. The following equations, represent the formation of the ligand and the complexes:

\[
\text{(OHH)₃C₆H₃CSSCH}_2\text{COOH+CH₃CONH₂} \rightarrow \text{NaOH} \quad \text{AcOH} \\
\text{(OHH)₃C₆H₃CSSCH}_2\text{COOH+CH₃CONH₂} \rightarrow \text{NaOH} \quad \text{AcOH}
\]

\[
\text{[M(OC)]₃(H₂O)₃]} + 2\text{H₂Bptbh} \rightarrow \text{MeOH} \quad \text{EtOH} \quad \text{[M(Bptbh)]₂} + 2\text{H₂OAc} + n\text{H₂O}
\]

\[
\text{M} = \text{Cu}^{II}, \text{Zn}^{II}, \text{Cd}^{II}; \quad n = 1, 2, 2
\]

\[
\text{[VO(acac)]₂+H₂Bptbh} \rightarrow \text{MeOH} \quad \text{[VO(Bptbh)] + 2Hacac}
\]

\[
\text{[Fe(acac)]₂+2H₂Bptbh} \rightarrow \text{MeOH} \quad \text{[Fe(HBptbh)₂(acac)] + 2Hacac}
\]

[VO(Bptbh)] shows a magnetic moment of 1.78 BM indicating the presence of one unpaired electron and it exhibits two bands at 11900 and 14290 cm⁻¹ corresponding to the \( ^2B_2 \rightarrow ^2E_1 , ^2A_1 \) transitions, respectively, in the square pyramidal geometry. A magnetic moment of 5.90 BM for [Fe(HBptbh)₂(acac)] and presence of a band at 17150 cm⁻¹ assigned to the \( ^6A_{1g} \rightarrow ^4T_{2g} \) transition suggests an octahedral geometry around ion(III). [Cu(HBptbh)₂] shows a magnetic moment of 2.01 BM as expected for the presence of one unpaired electron and it exhibits a \( d-d \) band at 12500 cm⁻¹ due to the envelope of \( ^4T_{1g} \rightarrow ^2T_{2g}, ^4T_{1g} \) transition usually observed (for square planar Cu(II) complexes). Other bands in the region of 22000-30770 cm⁻¹ in the complexes are assigned to the charge-transfer and intra ligand transition.

The room temperature ESR spectra of [VO(Bptbh)] is typical of oxovanadium(IV) complexes, with well resolved sixteen line hyperfine structure (~100 atom% \(^{51}\)V, I = 7/2). The measured parameters are: \( g_∥ = 1.922, g_\perp = 1.933, A_∥ = 180.0×10^{-4}\text{cm}^{-1} \) and \( A_\perp = 80.00×10^{-4}\text{cm}^{-1} \). The observed order in spin Hamiltonian parameters \( (g_∥ > g_\perp > A_∥ > A_\perp) \) suggest that the unpaired electron is largely in the \( d_∥ \) orbital with a square pyramidal structure around oxovanadium(IV). The solid state ESR spectrum of [Fe(Bptbh)₂(acac)] shows a broad signal with \( g_∥ = 2.060 \) for an octahedral Fe(II). The solid state ESR spectrum of [Cu(HBptbh)₂] yields two absorptions with \( g_∥ \) and \( g_\perp \) values of 2.222 and 2.067, respectively, for square planar Cu(II) complex.

The IR spectrum of H-Bptbh in KBr shows bands at 3370 and 3310 cm⁻¹ due to presence of two NH groups. A band also appears at 3280 cm⁻¹ due to \( \nu(\text{OH}) \) of the ligand. The bands at 1641, 1452, 1379, 891 and 1000 cm⁻¹ are assigned to \( \nu(\text{C}⁻\text{O}) \), thioamide I [\( \nu(\text{NH}) + \nu(\text{CN}) \)], thioamide II [\( \nu(\text{CN}) + \nu(\text{NH}) \)], \( \nu(\text{C}⁻\text{S}) \) and \( \nu(\text{N}⁻\text{N}) \) modes respectively. In the spectra of [M(HBptbh)₂] (M = Cu(II), Zn(II), Cd(II)) and

<p>| Table 1—Analytical data and physical properties of the complexes of N-benzyol-N'-p-hydroxythiobenzhydrazine |
|---------------------------------|---|---|---|---|---|---|---|</p>
<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour/Yield (°C)</th>
<th>M.P. °C</th>
<th>Found (Calcd. %)</th>
<th>M</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>( \mu_{\text{eff}} ) (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-Bptbh</td>
<td>Cream (80)</td>
<td>126</td>
<td>—</td>
<td>61.16</td>
<td>4.36</td>
<td>10.15</td>
<td>11.64</td>
<td>11.75</td>
<td>1.78</td>
</tr>
<tr>
<td>[VO(Bptbh)]</td>
<td>Brown &gt;360</td>
<td>13.19</td>
<td>50.01</td>
<td>2.72</td>
<td>8.30</td>
<td>9.60</td>
<td>—</td>
<td>5.90</td>
<td></td>
</tr>
<tr>
<td>[Fe(HBptbh)₂(acac)]</td>
<td>Brown (50)</td>
<td>8.04</td>
<td>56.90</td>
<td>3.80</td>
<td>8.09</td>
<td>9.30</td>
<td>—</td>
<td>5.90</td>
<td></td>
</tr>
<tr>
<td>[Cu(HBptbh)₂]</td>
<td>Black &gt;360</td>
<td>10.37</td>
<td>55.32</td>
<td>3.50</td>
<td>9.11</td>
<td>10.47</td>
<td>—</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td>[Zn(HBptbh)₂]</td>
<td>Off-white (45)</td>
<td>10.52</td>
<td>56.48</td>
<td>3.57</td>
<td>9.15</td>
<td>10.47</td>
<td>—</td>
<td>Diamagnetic</td>
<td></td>
</tr>
<tr>
<td>[Cd(HBptbh)₂]</td>
<td>Yellow (40)</td>
<td>17.24</td>
<td>50.01</td>
<td>3.30</td>
<td>8.41</td>
<td>9.67</td>
<td>—</td>
<td>Diamagnetic</td>
<td></td>
</tr>
</tbody>
</table>
[Fe(HBptbh)(acac)] the presence of a band in the range of 3305-3321 cm\(^{-1}\) due to \(v(\text{NH})\), suggests loss of one \(-\text{NH}^-\) proton \textit{via} enolization/thioenolization. A ligand band at 1641 cm\(^{-1}\) remains practically unchanged in the complexes suggesting non-involvement of carbonyl oxygen in bonding. The \(v(\text{C} \equiv \text{S})\) band at 891 cm\(^{-1}\) in the ligand is absent in the complexes but a new band due to \(v(\text{C} \equiv \text{S})\) mode appears at 752-761 cm\(^{-1}\), suggesting bonding through the thiolato sulphur\(^{13}\). A positive shift of 25 cm\(^{-1}\) in \(v(\text{N} \equiv \text{N})\) shows bonding through one hydrazinic nitrogen. Thus, the ligand is acting as an uninegative bidentate, bonded through thiolato sulphur and one hydrazinic nitrogen. In addition, the spectrum of [Fe(HBptbh)(acac)] shows bands at 2920, 1420 and 1330 cm\(^{-1}\) assigned to \(v(\text{CH})\), \(v\text{CH} + v(\text{C-C})\) and \(\delta(\text{CH})\) modes, respectively which are very close to the bands reported for a chelated acetylacetone group\(^8\).

In the IR spectrum of [VO(Bptbh)], the bands due to \(v(\text{NH})\), \(v(\text{C}=\text{O})\) and \(v(\text{C} \equiv \text{S})\) modes are absent, but two new bands appear at 1601 and 760 cm\(^{-1}\) due to \(v(\text{N}=\text{C})\) of \(\text{NCO}\) and \(v(\text{C} \equiv \text{S})\) modes, respectively, suggesting removal of both \(-\text{NH}^-\) protons \textit{via} enolization and thioenolization and bonding of the resulting enolic oxygen and thiolato sulphur takes place with the metal ion. Furthermore, the thiouamide I, II and \(v(\text{N} \equiv \text{N})\) bands in the free hydrazide undergo positive shifts suggesting involvement of thiolato sulphur and both the hydrazinic nitrogens in bonding in addition to the enolic oxygen. Thus, the ligand acts as a binegative tetradentate in the above complex.

The \(^1\text{H}\) NMR spectrum of the ligand shows three signals at \(\delta\) 9.66, 10.09 and 11.53 ppm due to the presence of \(-\text{NH}(\text{O})\), \(-\text{NH}(\text{S})\) and \(\text{OH}\) protons, respectively, which disappear on \(\text{D}_2\text{O}\) exchange. Phenolic ring proton appear at 8.0 (t, 1H), 6.90 (s, 2H) and 6.80 (s, 1H) while the benzene ring protons appear at \(\delta\) 7.63 (d, 1H), 7.53 (s, 2H) and 7.16 (s, 2H). [Zn(HBptbh)]\(_2\) shows only one NH signal at \(\delta\) 9.60 due to \(-\text{NH}(\text{O})\) suggesting removal of \(-\text{NH}(\text{S})\) proton \textit{via} thioenolization, and bonding through thiol sulphur\(^{15}\). Due to poor solubility \(^1\text{C}\) NMR spectra could not be recorded.

On the basis of physico-chemical studies and the foregoing discussion, Structure II is proposed for the complexes.

H\(_2\)Bptbh was identified by its FAB mass spectrum which shows many peaks due to various fragments. The spectrum shows the molecular ion peak at \(m/z = 272\). Other peaks at \(m/z = 240, 254, 120\) and 105 correspond to \((\text{OH})\text{C}_6\text{H}_5\text{CN}_2\text{COC}_6\text{H}_5\), \((\text{OH})\text{C}_6\text{H}_5\text{CN}_2\text{SCS}_6\text{H}_5\), \(\text{C}_6\text{N}_4\text{CONH}_2\) and \(\text{C}_6\text{H}_5\text{C}=\text{O}\) fragment, respectively, obtained from the ligand.

Mössbauer spectra of [Fe(HBptbh)(acac)] at room temperature and at liquid nitrogen temperatures have been studied. The spectra shows a doublet at both temperatures. The \(\delta\) and \(\Delta E_q\) values are 0.358 and 0.613 mms\(^{-1}\), respectively, at room temperature, while these values at liquid nitrogen temperature are 0.448 and 0.645 mms\(^{-1}\) respectively, which are indicative of high spin \(S = 5/2\) state of iron(III) with a distorted octahedral geometry.

[VO(Bptbh)] and [Cd(HBptbh)] show conductivity at room temperature, while [Fe(HBptbh)(acac)] shows conductivity at 343 K. Other complexes were found to be insulators. The plot of \(\text{ln} \text{R} \text{vs} 1/T\) show that the conductivity increases with an increase in temperature indicating their semiconducting
behaviour and the plot is almost linear. The band gap evaluated from the plot using the relationship: $2.303 \times 8.314 \times 10^{-5} \times \text{slope}$ was found to be 0.44, 0.75 and 0.47 eV for $[\text{VO(Bptbh)}]$, $[\text{Fe(HBptbh)}_{2}(\text{aca})]$ and $[\text{Cd(HBptbh)}_{2}]$, respectively, which indicate their potential to be used as sensitizer for wide band-gap semiconductor electrodes such as ZnO, TiO$_2$, SnO$_2$, etc., a component of dye-sensitized photoelectrochemical cells for practical applications such as solar cells, etc. Furthermore, the lower conductivity of the complexes show weaker intermolecular contact and less extended delocalization and rules out any possibility of partial oxidation of central metal producing higher conductivity.

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References