Complexes of Ti(III), oxovanadium(IV), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) with gallacetophenone phenylhydrazone

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The complexes of Ti(III), oxovanadium(IV), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) with gallacetophenone phenylhydrazone (GAPPH) have been synthesized and characterised by analytical, conductivity, thermal, magnetic, infrared, electronic and ESR data. All the complexes have 1:2 (metal:ligand) stoichiometry. All the complexes are non-electrolytes in dimethylformamide, except Ti(III) complex which is 1:1 electrolyte. The infrared spectral data of the metal complexes indicate that GAPPH acts as a mononegative bidentate ligand coordinating through oxygen of o-hydroxy group and nitrogen of azomethine group. The electronic spectral data suggest that Ti(III) and Fe(II) complexes are octahedral, oxovanadium(IV) complex is tetragonal and Ni(II) and Cu(II) complexes are square-planar. The Co(II), Zn(II) and Hg(II) complexes are tetrahedral.

Phenylhydrazones of o-hydroxy aldehydes and ketones have been used as reagents in gravimetric estimation. Generally, these reagents also act as good ligating agents. Though gallacetophenone phenylhydrazone (GAPPH) has been used as an analytical reagent, its complexes are not reported. This prompted us to prepare the complexes of Ti(III), oxovanadium(IV), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II) with GAPPH.

Results and discussion
All the complexes are stable at room temperature, non-hygroscopic, insoluble in water and many of the common organic solvents but are soluble in DMF and DMSO. The analytical data of the complexes (Table 1) indicate their composition as $M(GAPPH)_2$ where $M = Ti(III)$, oxovanadium(IV), Fe(II), Co(II), Ni(II), Cu(II), Zn(II) and Hg(II). However, the Ti(III) and Fe(II) complexes were found to be associated with two molecules of water and the oxovanadium(IV) complex with one molecule of water. The molar conductivities of 10⁻³ $M$ solutions of all the complexes, except the Ti(III) complex were found to be in the range 10⁻¹⁵ ohm⁻¹ cm² mol⁻¹ indicating their non-ionic nature. The Ti(III) complex showed a value of 80 ohm⁻¹ cm² mol⁻¹ indicating its 1:1 nature.
The electronic spectrum of the ligand exhibits a strong band around 37000 cm\(^{-1}\) and a shoulder at 36000 cm\(^{-1}\), assignable to the \(n \rightarrow \pi^*\) and \(\pi \rightarrow \pi^*\) transitions respectively. The electronic spectrum of Ti(III) complex exhibits one band at 15000 cm\(^{-1}\), which may be assigned to \(2T_{2g} \rightarrow E_g\) transition, characteristic of octahedral geometry. The oxovanadium(IV) complex shows two bands at 12000 and 18600 cm\(^{-1}\), which may be due to \(2B_{2g} \rightarrow 2E_g\) and \(2B_{2g} \rightarrow 2A_{1g}\) transitions respectively characteristic of distorted octahedral of tetragonal geometry. In the case of Fe(II) complex the bands observed at 16600 and 34500 cm\(^{-1}\) correspond to the transition \(5T_{2g} \rightarrow 5E_g\) and charge-transfer respectively indicating the octahedral geometry around Fe(II).

Reflectance spectrum of Co(II) complex shows two bands at 11250 and 15350 cm\(^{-1}\) due to \(4A_1g(F) \rightarrow 4T_{1g}(F)\) and \(4A_2g(F) \rightarrow 4T_{1g}(P)\) transitions characteristic of tetrahedral geometry. The electronic spectrum of Ni(II) complex is characterised by a broad peak centered at 21000 cm\(^{-1}\), which may be due to \(1A_{1g} \rightarrow 1A_{1g}\) transition, suggestive of square-planar geometry. The Cu(II) complex shows strong bands around 16000 and 22000 cm\(^{-1}\) assignable to \(2B_{1g} \rightarrow 2B_{2g}\) and \(2B_{1g} \rightarrow 2E_g\) transitions respectively characteristic of square planar geometry.

The magnetic moment values are given in Table 1. The Ti(III), oxovanadium(IV) and Cu(II) complexes are found to be paramagnetic with magnetic moment values corresponding to one unpaired electron. The values obtained for the Fe(II) and Co(II) complexes are in the ranges expected for octahedral and tetrahedral geometries respectively. Ni(II) complex is diamagnetic, which is characteristic of square planar geometry.

The ESR spectrum of Cu(II) complex in solid state at room temperature exhibits two peaks; the one at higher field is of greater intensity than that at low field. From the spectrum, the values of \(g\) and \(g_1\) have been calculated to be 2.20 and 2.05 G respectively by using Kneubuhl's method. The observed \(g\)-values point to the presence of unpaired electron predominantly in the \(d_{x^2-y^2}\) orbital. The complex also shows anisotropic ESR spectrum with \(g > g_1\), which is characteristic of square planar and tetragonal geometry (\(d_{x^2-y^2}\) ground state). Kivelson and Neiman have indicated that \(g\) is a moderately sensitive parameter for predicting covalency. For covalent environment...

### Table 1 — Analytical and magnetic data of the complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Found (Calc.) %</th>
<th>Magnetic moment (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ti(GAPPH)(_2)(H(_2)O)(_3)]Cl</td>
<td>7.05 (8.42)</td>
<td>52.68 (4.02)</td>
</tr>
<tr>
<td></td>
<td>(7.56) (8.84)</td>
<td>(53.05) (4.13)</td>
</tr>
<tr>
<td>[VO(GAPPH)(_2)(H(_2)O)(_2)]</td>
<td>8.09 (9.23)</td>
<td>56.72 (4.44)</td>
</tr>
<tr>
<td></td>
<td>(8.50) (9.35)</td>
<td>(56.10) (4.37)</td>
</tr>
<tr>
<td>[Fe(GAPPH)(_2)(H(_2)O)(_3)]</td>
<td>9.02 (9.12)</td>
<td>57.00 (4.02)</td>
</tr>
<tr>
<td></td>
<td>(9.21) (9.24)</td>
<td>(56.46) (4.32)</td>
</tr>
<tr>
<td>[Co(GAPPH)(_2)]</td>
<td>10.05 (9.39)</td>
<td>58.11 (4.82)</td>
</tr>
<tr>
<td></td>
<td>(10.28) (9.77)</td>
<td>(58.64) (4.57)</td>
</tr>
<tr>
<td></td>
<td>(10.24) (9.77)</td>
<td>(58.67) (4.57)</td>
</tr>
<tr>
<td>[Cu(GAPPH)(_2)]</td>
<td>10.78 (9.39)</td>
<td>58.70 (4.68)</td>
</tr>
<tr>
<td></td>
<td>(10.99) (9.69)</td>
<td>(58.18) (4.53)</td>
</tr>
<tr>
<td>[Zn(GAPPH)(_2)]</td>
<td>10.89 (9.02)</td>
<td>57.54 (4.05)</td>
</tr>
<tr>
<td></td>
<td>(10.27) (9.66)</td>
<td>(57.99) (4.52)</td>
</tr>
<tr>
<td>[Hg(GAPPH)(_2)]</td>
<td>27.69 (7.44)</td>
<td>46.71 (3.28)</td>
</tr>
<tr>
<td></td>
<td>(28.05) (7.83)</td>
<td>(47.03) (3.66)</td>
</tr>
</tbody>
</table>

All the complexes, except those of Ti(III), oxovanadium(IV) and Fe(II) were found to be thermally stable up to 200°C indicating that they are non-hydrated. The TG curves of Ti(III) and Fe(II) complexes showed mass loss in the temperature range 140-160°C, corresponding to loss of two water molecules and TG curve of oxovanadium(IV) complex showed mass loss at 150°C corresponding to loss of one water molecule. These observations show the coordinated nature of the water molecules. The thermograms of all the complexes show sharp peaks above 200°C associated with the loss of the organic part. The final products of decomposition, as computed from the thermograms of metal complexes, correspond to metal oxides only.

A band at 1235 cm\(^{-1}\) in the IR spectrum of the ligand, assignable to \(\nu(C - O)\) (phenolic), undergoes a positive shift in the complexes. This indicates the deprotonation of a \(\sigma\)-hydroxy group and subsequent bonding through oxygen. A band around 3500 cm\(^{-1}\), in the ligand as well as in the complexes, may be assigned to the \(\nu\)OH mode of OH groups present in the ring. A band observed at 1600 cm\(^{-1}\) in the free ligand is due to the \(\nu(C = N)\) mode. This undergoes lowering in the spectra of complexes by 50 cm\(^{-1}\) indicating that the nitrogen of azomethine group is involved in the coordination. The IR spectra of the Ti(III), oxovanadium(IV) and Fe(II) complexes display peaks a 3600-3300, 1650 and 800-700 cm\(^{-1}\) due to the presence of coordinated water. Further, a band observed at 900 cm\(^{-1}\) in oxovanadium(IV) complex has been attributed to \(\nu(V = O)\). The participation of nitrogen and oxygen in coordination in all the complexes is further supported by the appearance of \(\nu(M - N)\) and \(\nu(M - O)\) modes at 500 and 400 cm\(^{-1}\) respectively.
ments $g_i$ is $>2.3$ and for ionic environments $g_i$ is usually $<2.3$. Thus, the present $g_i$ value indicates that the metal-ligand bonding in the copper complex is covalent\textsuperscript{17}. The axial symmetry parameter ($G$) for the complexes is found to be greater than 4 (4.15) indicating the absence of interaction between copper centers in the solid state\textsuperscript{18,19}.

Further, the orbital reduction parameters $r_1^2$, $r_2^2$, $\gamma^2$, $\alpha^2$, $\beta^2$ and $\beta^2$ have been calculated. The $\alpha^2$ value is found to be 0.56 which indicates the presence of appreciable in-plane covalency. As $r_2^2 > r_1^2$ in the complex, it indicates that the ligand is in-plane $\pi$-bonded\textsuperscript{10}. The spin-orbit coupling constant for the complex is found ($-383$ cm$^{-1}$) to be less than that of the free metal ion suggesting considerable mixing of ground and excited terms. The $g$-value is also useful for calculating the magnetic moment ($\mu$) of the complex and the calculated value is in good agreement with the experimental one.

Based on the analytical and spectral data, structure\textsuperscript{(1)} is assigned to the complexes.

References