Synthesis & Structural Studies of Oxovanadium(IV), Manganese(II), Iron(II), Cobalt(II), Nickel(II) & Copper(II) Complexes with New Tridentate Schiff Bases having ONO & ONN Donor Systems

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Two new schiff bases have been synthesized by the condensation 6-chloro-4-hydroxy-3-acetylcoumarin with α-aminophenol (Cl-HACAP) and 2,6-diaminopyridine (Cl-HACDPy). Complexes of oxovanadium(IV), manganese(II), iron(II), nickel(II) and copper(II) with Cl-HACAP and Cl-HACDPy have been prepared. Molar conductance measurements indicate that the complexes are non-electrolytic in nature. The analytical data show that the metal to ligand ratio in all the complexes is 1:1. The complexes are characterized on the basis of analytical data, conductivity measurements, TG analysis, magnetic moment measurements and spectral data. The IR data show that the ligands act as tridentate ONO and ONN donor systems.

Although transition metal complexes of 6-chloro-4-hydroxy-3-acetylcoumarin are known, comparatively much less work has been done on the transition metal complexes of the schiff bases derived from it. Hence we thought it of interest to prepare schiff bases of 6-chloro-4-hydroxy-3-acetylcoumarin with two different amines, i.e., α-aminophenol and 2,6-diaminopyridine, and study their complexing behaviour with oxovanadium(IV), manganese(II), iron(II), nickel(II) and copper(II).

Materials and Methods
All the chemicals used were of AR quality. 2,6-Diaminopyridine (Riedel), malonic acid (Riedel), nitrobenzene (Wilson Lab), p-chlorophenol (E. Merck) and aluminium chloride (Ranbaxy) were used in the preparation of ligands.

The schiff bases were prepared by refluxing 6-chloro-4-hydroxy-3-acetylcoumarin with α-aminophenol (1:1, in ethanol) and 2,6-diaminopyridine (1:1, in methanol) for one hour when the two ligands were obtained as colourless solids. Their purity was checked by TLC and m.p. determination: Cl-HACAP (m.p. 230±2°C), Cl-HACDPy (m.p. 200-5°C).

The metal chelates of Cl-HACAP were synthesized by refluxing ethanolic solutions of respective metal chlorides (0.01 mol) and the ligand (0.01 mol) for about 2-3 hr and keeping the reaction mixtures overnight. The metal chelates of Cl-HACDPy were synthesized by refluxing the methanolic solutions of respective metal chlorides (0.01 mol) and the ligand (0.01 mol) for about an hour. The respective metal chelates that separated out were filtered, washed successively with hot solvent followed by pet. ether (60-80°C) and dried in vacuo. In the case of oxovanadium(IV) and Fe(II) complexes, vanadyl sulphate and aqueous ethanolic solution of ferrous ammonium sulphate were used.

The complexes were analysed for metal contents employing standard procedures after destroying the organic matter with a mixture of nitric and hydrochloric acids. Sulphur and chlorides were estimated as BaSO4 and AgCl respectively. Nitrogen was determined by microanalysis.

Electrochemical conductances of $1 \times 10^{-3} \text{M}$ solutions of all complexes in DMF were measured by conductivity meter model D1-909 (Digism electronics) and digital direct reading conductivity meter 304 (Systronics). The thermogravimetric analysis was carried out on a manually operated thermo-balance, with the heating rate of 5° per minute. The magnetic susceptibilities of the complexes were determined by Gouy method using Hg[Co(NCS)4] as the calibrant and the experimental magnetic susceptibilities were corrected for diamagnetism. Electronic spectra were recorded in nujol mull at room temperature on UV-visible spectrophotometer DMR-21 and ESR spectra were recorded on a JEOL-JES-F3X spectrometer. The infrared spectra of the ligand and the complexes were recorded in KBr on a Perkin-Elmer spectrophotometer model 627.

Results and Discussion
All the complexes reported here are coloured and stable towards air and moisture. Most of them are insoluble in common organic solvents
Table 1 - Analytical Data of Complexes of Cl-HACAP & Cl-HACDPy

<table>
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<tr>
<th>Ligand/Complex</th>
<th>Metal</th>
<th>Found (Calc) %</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>Cl</th>
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<td>C₆H₆O₇NCl</td>
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<td>VO(II)-[Cl-HACAP]</td>
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<td>Cl-HACDPy</td>
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<td>(3.640)</td>
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<td>15.25</td>
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<td>(CuCl₂(H₂O)₆NCl)</td>
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<td>(41.50)</td>
<td>(3.242)</td>
<td>(9.078)</td>
<td>(15.1)</td>
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</table>

*Satisfactory S analysis was also obtained.

Both, Cl-HACAP and Cl-HACDPy can exhibit tautomeric forms (I-IV).

The ligands Cl-HACAP and Cl-HACDPy can exist in equilibrium mixtures of lactone and chromone forms or may prefer only one of the forms depending upon the energy difference amongst these tautomeric forms.

The IR spectrum of Cl-HACAP shows a strong broad band in the region 3050-3300 cm⁻¹ assignable to inter- and intra-molecular hydrogen-bonded νOH. Three intense bands observed at 1670, 1590, 1460 cm⁻¹ are assigned to νC=O (chromone), νC=N and νC=O respectively. The IR band for νC=O in chromone form generally appears in the range 1650-1670 cm⁻¹ while νC=O of lactone form appears in the range 1700-1720 cm⁻¹. Since the ligand shows the band at 1670 cm⁻¹, it is concluded that the ligand in the solid state has chromone structure. In the complexes, the behaviour of the ligand is somewhat different. In oxovanadium(IV) and Cu(II) complexes it is present in the lactone form and in the rest of the complexes it is present in the chro-

and sparingly soluble in DMF, dioxane and DMSO.

The conductance values of 1×10⁻³ M solutions of all the complexes in DMF (2.1-10.1 mhos cm⁻² mol⁻¹), show their non-electrolytic behaviour.

The analytical data of the ligands and complexes are given in Table 1 which show that the metal to ligand ratio in all the complexes is 1:1.

TG and DT analyses were carried out to confirm the presence of coordinated water in the complexes of Cl-HACAP. The mass loss was found to be equivalent to two moles of water in the case of Mn(II), Fe(II), Co(II) and Ni(II) complexes and it was a two-step process. Two endothermic peaks in each case have been obtained. [Mn(II) at 145° and 160°C; Fe(II) at 140° and 165°C; Co(II) at 130°C and 170°C; and Ni(II) at 135°C and 165°C].

In the case of Cl-HACDPy complexes the thermogravimetric analysis shows that Cu(II) and Fe(II) complexes have two moles of coordinated water while Mn(II), oxovanadium(IV), Co(II) and Ni(II) complexes have only one mole of water.
In the spectra of the complexes the absence of a broad band at 3050-3300 cm\(^{-1}\) indicates the cleavage of the hydrogen bond, deprotonation of the phenolic oxygen, and its coordination to the metal ion. The spectra of Mn(II), Fe(II), Co(II) and Ni(II) complexes show a broad absorption in the region 3320-3400 cm\(^{-1}\) which indicates the presence of coordinated water\(^5\) the presence of which is also confirmed by TG analysis. In the case of oxovanadium(IV) and Cu(II) complexes no such band is observed indicating the absence of coordinated water. A strong band at 1460 cm\(^{-1}\) assigned to vC-O in the free ligand, is resolved into two peaks in the complexes. The lower energy band is assigned to vC-O of coumarin moiety while the higher energy one is attributed to vC-O of benzene moiety\(^6\). Both the bands occur at higher frequencies compared to vC-O in the free ligand. This indicates participation of both the phenolic oxygens in coordination subsequent to deprotonation\(^7,8\). As the shift in case of vC-O on benzene moiety is high (~40 cm\(^{-1}\)) it is assumed that the oxygen of this group acts as a bridging centre\(^9\). The positive shift in vC=N (15-20 cm\(^{-1}\)) in complexes confirms the participation of the azomethine nitrogen in complex formation\(^10,11\). A new band in oxovanadium(IV) complex at 900 cm\(^{-1}\) is attributed to vV=O\(^12\). The extra bands around 580 and 460 cm\(^{-1}\) are assigned to vM=N and vM=O modes respectively\(^13,15\). The changes in the IR spectra of the complexes indicate the formation of metal chelates.

A broad absorption is observed at 3050-3300 cm\(^{-1}\) in the IR spectrum of the ligand Cl-HACDPy which is assigned to inter and intra-molecular hydrogen bonded vOH vibration. The bands due to v\(_{as}\)NH\(_2\) and v\(_{s}\)NH\(_2\) could not be pinpointed. These might have been overlapped with the broad absorption. Intense bands at 1720,

1610, 1430 cm\(^{-1}\) are assignable to vC=O (lactone), vC=N\(^14\) of azomethine and vC=O\(^6\) (phenolic) respectively. The bands between 1570 and 1420 cm\(^{-1}\) are ascribed to vC=N (ring) and vC=C of pyridine ring\(^9\) respectively\(^15,16\). In the IR spectra of all the complexes a broad band is observed in the region 3150-3500 cm\(^{-1}\) which is assigned to overlapping of the bands due to vNH\(_2\) and coordinated water. The presence of coordinated water is confirmed by TG and DT analysis and by the presence of new peaks at 820-840 cm\(^{-1}\) in the complexes. The absence of strong band in the region of 3500-3600 and appearance of a new peak at about 1440-1460 cm\(^{-1}\), assignable to vC-O (phenolic), indicate cleavage of the hydrogen bonding, deprotonation of hydroxyl group and subsequent coordination of oxygen with metal ion. The downward shift in vC=N (10-15 cm\(^{-1}\)) shows the participation of nitrogen of azomethine group in complexation\(^17,18\). There is a downward shift (35-45 cm\(^{-1}\)) in vC=O (lactone) in the complexes of Mn(II), Co(II) and Ni(II) which favours the participation of oxygen of vC=O (lactone) forming polymeric species\(^19,20\). In rest of the complexes there is no change in vC=O (lactone). Considerable changes have been noticed in the bands in the range 1560-1430 cm\(^{-1}\) which are consistent with the participation of nitrogen of the pyridine ring in coordination\(^18\). A new peak at 900 cm\(^{-1}\) is assigned to vV=O\(^5\). The presence of M-O and M-N bonding is confirmed by new peaks observed in the region 600-400 cm\(^{-1}\) (ref. 21). The presence of chloride was confirmed by analytical data.

From the IR data it has been concluded that Cl-HACDPy behaves as a monobasic tridentate ligand, coordinating to metal ions through the deprotonated phenolic oxygen, the azomethine nitrogen and the nitrogen of pyridine ring.

The observed magnetic moment of oxovanadium(IV)-[Cl-HACAP] complex is 1.5 B.M. The low magnetic moment may be attributed to antiferromagnetic coupling of spin\(^22\). The electronic spectrum of this complex exhibits two bands at 12048 and 26315 cm\(^{-1}\) which may be assigned to the transitions \(2b_2\rightarrow 2e\) and \(2b_2\rightarrow 2a_1\) respectively in square-pyramidal geometry. The oxovanadium(IV)-[Cl-HACDPy\(_2\)SO\(_4\)] complex possesses room temperature magnetic moment value of 1.79 B.M. Its electronic spectrum exhibits two bands at 14285 and 16000 cm\(^{-1}\) which are assigned to the transitions \(b_2\rightarrow e\) and \(b_2\rightarrow a\) respectively in a distorted octahedral geometry\(^23\).

The room temperature magnetic moment of Mn(II)-[Cl-HACAP\(_2\)H\(_2\)O] complex is 4.57 B.M.
The observed moment is low compared to spin-only value (5.92 B.M.) for high-spin Mn(II) complexes. This may be due to the presence of very small amount of Mn(III) species and strong metal-metal interaction in the complexes. The Mn(II) complex displayed very weak absorption and it was difficult to assign them to definite transitions. The Mn(II)[Cl-HACDPy.Cl.H2O] complex shows the magnetic moment of 5.86 B.M. which is slightly low when compared to spin-only value of 5.92 B.M. The low value may be due to the presence of Mn(III) species or spin-exchange in the solid phase. Its electronic spectrum exhibits several weak absorption in the range 12200-25000 cm⁻¹. A polymeric octahedral structure is proposed for Mn(II) complex.

The observed room temperature magnetic moment of Fe(II)-[Cl-HACAP.2H2O] complex is 4.97 B.M. which is low compared to the expected magnetic moment. The low value may suggest strong metal-metal interaction. The visible spectrum of Fe(II) complex exhibits a broad band at 13000 cm⁻¹ assignable to ⁵T₂g → ⁵E₇ transition. The magnetic moment of Fe(II)-[Cl-HACDPy.2H₂O.SO₄] was found to be 5.24 B.M. which is well within the range of high-spin octahedral Fe(II) complexes. Fe(II) complex shows a very weak absorption at 12275 cm⁻¹ which may be assigned to the transition ⁵T₂g → ⁵E₇ under octahedral geometry.

The Co(II)-[Cl-HACAP.2H₂O] complex possesses a magnetic moment value of 4.5 B.M. which is in agreement with the value required for three unpaired electrons. Its electronic spectrum shows three bands at 8510, 18510 and 21276 cm⁻¹ which may be assigned to ⁴T₁g→⁴T₂g (F), ⁴T₁g (F)→³A₂g (F), ⁴T₁g (F)→⁴T₁g (P) respectively. The positions of the observed bands agree with those of the other reported Co(II) octahedral complexes. The Co(II)-[Cl-HACDPy.Cl.H₂O] complex exhibits magnetic moment of 4.24 B.M. suggesting high-spin octahedral configuration. This Co(II) complex shows two main bands at 25640 and 18500 cm⁻¹ which are assignable to the transitions ⁴T₁g (F)→⁴T₂g (F) and ⁴T₁g (F)→⁴T₂g (P) respectively in a high-spin octahedral configuration.

The observed room temperature magnetic moment of Ni(II)-[Cl-HACAP.2H₂O] complex is 2.605 B.M., close to the value required for octahedral structure. Its electronic spectrum shows three bands at 9523, 16000 and 26315 cm⁻¹ which can be assigned to the transitions ³A₂g (F)→³T₁g (F), ³A₂g (F)→³T₁g (F) and ³A₂g (F)→³T₁g (P) respectively. The observed magnetic moment value of Ni(II)-[Cl-HACDPyCl.H₂O] complex is 2.8 B.M. and its electronic spectrum shows three characteristic bands at 10526, 17540 and 27770 cm⁻¹ which are suggestive of octahedral geometry. The three bands are assigned to ³A₂g (F)→³T₁g (F), ³A₂g (F)→³T₁g (F) and ³A₂g (F)→³T₁g (P) transitions respectively.

The room temperature magnetic moment of Cu(II)-[Cl-HACAP] complex is 1.6 B.M. The low value of magnetic moment may be due to the metal-metal interactions due to the presence of bridging structure. The electronic spectrum of Cu(II) complex displays three bands at 13700, 14925 and 19420 cm⁻¹ which can be assigned to the transitions ²B₂g→²B₃g, ²B₂g→²A₁g and ²B₂g→²E₇ respectively under the square-planar geometry. The Cu(II)-[Cl-HACDPy.Cl.2H₂O] complex possesses a magnetic moment value of 1.8 B.M. which is well within the range of octahedral complexes. Its electronic spectrum exhibits a broad band at 13000-17000 cm⁻¹ which is assignable to the ²E₇→²T₂g transition in octahe-
dral geometry. The broadness of the band is due to the Jahn-Teller distortion operative for the $d^9$ configuration. A distorted octahedral geometry has been tentatively assigned. The ESR spectra of oxovanadium(IV) and Cu(II) complexes of Cl-HACAP show sharp bands corresponding to the $g_{av}$ value of 1.9650 and 2.068 which is resultant of $g_1$ and $g_2$. The $g_{av}$ values of the corresponding complexes with Cl-HACDPy are 1.989430 and 2.063431 respectively which are in agreement with the values required for one unpaired electron.

On the basis of analytical data, conductivity data, magnetic susceptibility measurements, TG and DT analysis and spectral data, structures V-VII are proposed for the present complexes.

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References