Dimeric Five- & Six-coordinated Complexes of Oxovanadium (IV) with Bi-, Tri- & Tetradeontate Ligands

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Picolinic acid hydrazide (PH), o-hydroxyacetophenone picolinoyl hydrazone (APH), isonicotinic acid hydrazide (INH) and o-hydroxyacetophenone isonicotinoyl hydrazone (A1H) form cationic and neutral five- and six-coordinated complexes with oxovanadium (IV) of the type \([\text{VO}_nX]_m\), where \(X = \text{Cl, Br, NO}_2\) and NCS. The complexes are characterised on the basis of elemental analyses, conductance, molecular weight, magnetic moment, electronic and infrared spectral data. PH and A1H act as tridentate, INH as bidentate and APH as tetradeontate ligands. The molecular weight, magnetic moment and infrared spectral studies indicate the dimeric nature of the complexes in which enolic oxygen acts as a bridge. Various metal-ligand vibrations are assigned in the far IR region. The electronic spectra of the complexes are consistent with the proposed stereochemistries. Various ligand-field parameters have been calculated using NSH Hamiltonian theory. The amounts of distortion from idealised \(C_{5v}\) and \(D_{2h}\) symmetries are calculated in terms of the ratio \(DT/DQ\) and these values indicate that the complexes are moderately distorted.

**TABLE 1 — ANALYTICAL DATA OF OXOVANADUM (IV) COMPLEXES OF PH, APH, INH AND A1H**

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour</th>
<th>Found (Calc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{VO(C}_2\text{H}_4\text{N}_2\text{O})\text{Cl}_2)</td>
<td>Greenish-blue (21.70) (17.87) (239.5)</td>
<td>467</td>
</tr>
<tr>
<td>(\text{VO(C}_2\text{H}_4\text{N}_2\text{O})\text{Br}_2)</td>
<td>Greenish-blue (18.26) (14.97) (284)</td>
<td>515</td>
</tr>
<tr>
<td>(\text{VO(C}_2\text{H}_4\text{N}_2\text{O})\text{NO}_2)</td>
<td>Reddish-brown (18.89) (21.46) (355)</td>
<td>520</td>
</tr>
<tr>
<td>(\text{VO(C}_2\text{H}_4\text{N}_2\text{O})\text{NCS}_2)</td>
<td>Bluish-green (19.79) (21.58) (520)</td>
<td>520</td>
</tr>
<tr>
<td>(\text{VO(C}_2\text{H}_4\text{O}_2\text{N})\text{Cl}_2)</td>
<td>Bluish-green (16.11) (13.42) (520)</td>
<td>520</td>
</tr>
<tr>
<td>(\text{VO(C}_2\text{H}_4\text{O}_2\text{N})\text{Br}_2)</td>
<td>Bluish-green (19.79) (21.46) (355)</td>
<td>520</td>
</tr>
<tr>
<td>(\text{VO(C}_2\text{H}_4\text{O}_2\text{N})\text{NO}_2)</td>
<td>Reddish-brown (19.91) (23.05) (355)</td>
<td>520</td>
</tr>
<tr>
<td>(\text{VO(C}_2\text{H}_4\text{O}_2\text{N})\text{NCS}_2)</td>
<td>Bluish-green (19.18) (21.06) (523)</td>
<td>523</td>
</tr>
<tr>
<td>(\text{VO(C}_2\text{H}_4\text{O}_2\text{N})\text{Cl}_2)</td>
<td>Bluish-green (15.72) (13.37) (641)</td>
<td>641</td>
</tr>
</tbody>
</table>

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by heating with conc. nitric acid and dissolving them in conc. HCl. The results were confirmed by igniting the complex in air and estimating the metal as pentoxide.

Microanalysis of C, H and N were carried out at IIT, Kanpur. The magnetic susceptibility at room temperature was determined by Guoy's method using copper sulphate pentahydrate as the calibrant.

The electronic spectra were recorded in nujol-mull on a Cary-14 recording spectrophotometer. The IR spectra (4000-650 cm$^{-1}$) were recorded in KBr on a Perkin-Elmer spectrophotometer 621 model and in nujol-mull (650-200 cm$^{-1}$) on Beckman IR-12 spectrophotometer. The molar conductance was measured in DMF on a Toshniwal conductivity bridge type CL01/01. The molecular weights of complexes were determined cryoscopically using water as the solvent.

Results and Discussion

The analytical data reveal 1:1 (metal-ligand) stoichiometry of the complexes. The conductivity measurements show non-electrolytic nature of all the complexes. The ratio of observed (determined cryoscopically in water) and calculated molecular weights lies between 1.81 and 2.10, which indicates dimeric nature of the complexes.

Infared spectra — The ligands show characteristic amide frequencies around 1670-1690, 1510-1530, 1240-1260, 660-670 and 480-500 cm$^{-1}$ assignable to amide-I ($\nu(CO)$), amide-II and amide-III ($\nu(CN)$ and $\delta$NH), amide-IV in-plane (C$\equiv$O) deformation and amide-VI, out-of-plane deformation modes, respectively.$^9$ The spectra of complexes do not show any characteristic frequencies of amide group, instead a sharp and strong band appears around 1595-1600 cm$^{-1}$ which is diagnostic of azine ($\geq C=\equiv N<\equiv C<\equiv$) group.$^8$ This change suggests that the oxygen of the amide group coordinates in enolic form through deprotonation. The presence of bands at 1530 and 1360 cm$^{-1}$ assignable to $\nu$NCO further confirm the enolisation of the ligand.$^9$ Spectra of PH and INH show bands at 3300-3350 and 3200-3250 cm$^{-1}$ while two bands at 3200 and 3050 cm$^{-1}$ are observed in the spectra of APH and AIH. These bands may be assigned to symmetric and asymmetric NH stretching modes, respectively. In addition, two bands appear around 1650 and 840 cm$^{-1}$ (in PH and INH only) which may be assigned to NH deformation coupled with the OCN antisymmetric vibrations. In the spectra of complexes of PH and INH, the NH bands show a downward shift and appear around 3180 and 3000 cm$^{-1}$ the band around 1650 cm$^{-1}$ disappears completely and the NH out-of-plane bending around 840 cm$^{-1}$ diminishes in intensity. All these changes show coordination of hydrazinic nitrogen.$^9$

The disappearance of phenolic (OH) stretching vibrations observed in free ligands APH and AIH around 3580 cm$^{-1}$, clearly indicates the loss of proton on coordination and formation of a new metal-oxygen bond.$^8$ The phenolic (C-O) stretching vibration in Schiff bases occurs as a strong band around 1280 cm$^{-1}$, which on chelation is raised to 1330-1355 cm$^{-1}$ in the spectra of complexes. This shift to higher energy on complexation indicates the coordination through (OH) group$^3$, which is further confirmed by the appearance of new bands around 440-465 cm$^{-1}$ assignable to $\nu$VO-O frequencies.$^9$ The magnetic properties (to be discussed later) and molecular weight determination indicate the magnetically condensed and dimeric nature of the complexes which can occur through phenoxide or enolic oxygen bridging. The band around 1540 cm$^{-1}$ in the spectra of all the ligands does not shift in the spectra of the complexes and this shows the absence of phenoxide bridging$^{13}$. The presence of new bands around 345-355 cm$^{-1}$ assignable to $\nu$VO-O (enolic) mode, appearing in comparatively lower region may be due to enolic oxygen bridging.$^3$

In the spectra of ligands APH and AIH, strong bands around 1580-1630 cm$^{-1}$ may be assigned to $\nu$C$=\equiv N$ and $\nu$C$=\equiv C$ vibrations$^{14,9}$, because these bands do not appear in the spectra of hydrazides. The spectra of complexes show a downward shift of 10-15 cm$^{-1}$ in these vibrations and are consistent with the coordination of azomethine nitrogen to the metal atom. This mode of coordination is further confirmed by the presence of new bands around 460-480 cm$^{-1}$, $\nu$VO-N (hydrazine) and $\nu$VO-N (azomethine) vibrations in the far IR spectra of the complexes.$^9$

All the free ligands show pyridine ring $\nu(C=\equiv C)$ and $\nu(C=\equiv N)$ vibrations in the regions 1585-1595 cm$^{-1}$ (band-I), 1570-1580 cm$^{-1}$ (band-II), $\sim 1450$-1490 cm$^{-1}$ (band-III) and 1435-1440 cm$^{-1}$ (band-IV), respectively.$^9$ The spectra of PH and APH complexes exhibit an upward shift of amide-I band which appears around 1605 cm$^{-1}$, an indication of coordination through pyridine nitrogen.$^9$

The bands around 795, 735, and 990 cm$^{-1}$ in the free ligands are assigned to $\gamma$(C-H), $\delta$(C-C) and ring breathing modes, respectively. The spectra of PH and APH complexes show various changes in these vibrations indicating the coordination through pyridine nitrogen.$^{17-20}$ This mode of coordination is further supported by the presence of new bands around 255-265 cm$^{-1}$ assignable to $\nu$O=V-N (pyridine) vibrations.

However, no significant changes are observed in the pyridine vibrations in the cases of INH and AIH complexes. This indicates that pyridine nitrogen does not take part in coordination. The bands around 950-970 cm$^{-1}$ appearing in the spectra of all the complexes are assigned to $\nu$V=O mode and are consistent with the terminal V=O group.

The new bands around 290 and 375 cm$^{-1}$ in the spectra of PH complexes, may be assigned to $\nu$(VO-Cl)$^{11}$ vibrations. Similar vibrations appear around 320 and 395 cm$^{-1}$ in the spectra of INH complexes and arecomparatively at higher energies due to the difference in stereochemistries of the two types of complexes. The $\nu$(VO-Br) vibrations are observed around 260-295 and 340-365 cm$^{-1}$ in these complexes. The changes observed in nitrate and thiocyanate complexes of PH and INH indicate monodentate nature of these ligands. The nitrate complexes show bands in the regions 1770-
1760 and 1755-1740 cm\(^{-1}\), which show that the nitrate group is coordinated to the metal atom and the small splitting is consistent with monodentate nature of the nitrate group\(^{39}\). Further, appearance of bands at 1535, 1395, 995 and 815 cm\(^{-1}\) assignable to asymmetric (\(\nu_s\)) and symmetric (\(\nu_s\)) modes of NO\(_2\) group, NO stretching (\(\nu_a\)) and planar rocking (\(\nu_d\)), respectively also confirm its monodentate nature. The weak bands around 220-240 cm\(^{-1}\) may be assigned to \(\nu VO-O\) mode of nitrate group. The thiocyanate complexes of PH and INH show bands around 2050, 870 and 460 cm\(^{-1}\) assignable to \(\gamma CN\), \(\gamma CS\) and \(\gamma NCS\) modes which also indicate the presence of N-bonded thiocyanate group\(^{10}\). A sharp band around 370-380 cm\(^{-1}\) in the spectra of complexes may be assigned to \(\nu(\gamma O=V-NCS)\).

Thus, it is evident from IR spectra that: (a) INH acts as a bidentate ligand coordinating through hydrazinic nitrogen and deprotonated enolic oxygen (which acts as a bridge), (b) PH acts as a tridentate ligand and it coordinates through pyridine nitrogen besides the above sites, (c) AH acts as a tridentate ligand coordinating through azomethine nitrogen as well as deprotonated enolic oxygen, the latter acting as a bridge, and (d) APH acts as a tetradeutate ligand coordinating through pyridine nitrogen besides the other sites as in AH. The halogen, nitrate and thiocyanate groups are present in the coordination sphere.

### Magnetic and electronic spectral studies

The magnetic moments of the complexes lie in the range 1.28-1.33 B. M. These values are much lower than the spin-only value (1.73 B. M.) predicted for oxovanadium(IV) complexes\(^{39}\). The observed magnetic moments are comparable with that of Cu(II) acetate (1.38 B. M.) which is binuclear antiferromagnetic. Thus, it seems reasonable to assume that the sub-normal magnetic moments arise from antiferromagnetic interactions\(^{34}\). The dimeric structure may be a consequence of oxygen bridged structure. Since phenoxy or V=O bridging is ruled out on the basis of IR spectra, it is plausible that the sub-normal magnetic moments may be due to spin coupling via super-exchange through the enolic oxygen atoms (vide infra).

The solution spectra of PH and APH complexes are very similar as are the spectra of INH and AH complexes. This similarity of spectra indicates that the structures of PH and APH complexes are similar and the same is true for INH and AH complexes. The solution spectra of PH and APH are characterised by a single band maximum around 17500-17700 cm\(^{-1}\) with inflexions around 13150-13250 cm\(^{-1}\) and 24150-24450 cm\(^{-1}\). The other bands are observed around 27400-27650 and 37700-37900 cm\(^{-1}\). The spectra of INH and AH complexes show bands in the regions 13700-13820, 16150-16260, 24740-24800 and 36100-36250 cm\(^{-1}\). A comparison of the latter spectra with the former indicates that band-I shifts to higher energy by \(\sim 1600\) cm\(^{-1}\) and band II moves to lower energy by \(\sim 1400\) cm\(^{-1}\). This observation is similar to that observed in the complexes of oxovanadium(IV) with 1,3-diamines, where a five-coordinated complex changes to six-coordinated environment. Moreover, the tetra- and tri-denticity of the ligands (APH and AH), dimeric nature and absence of anions in these complexes confirm the six- and five-coordinated geometries around the metal ion. A shift of \(\nu V=O\) to higher range in INH and AH as compared to PH and APH complexes also indicates an additional increase in axial (V=O) bonding for the five-coordinated complex\(^{39}\).

X-ray data\(^{36,37}\) also show that the loss of a donor molecule from sixth position increase the V=O bond order. On the basis of these observations, the transitions viz., \(2B_2 \rightarrow 2E\), \(2B_2 \rightarrow 2B_1\) would be expected to shift to higher and lower energies, respectively in five-coordinated complexes as compared to the six-coordinated complexes. The band at 24000 cm\(^{-1}\) may be assigned to the transition \(2B_2 \rightarrow A_1\). Similar bands have been observed in oxovanadium (IV) complexes with a variety of ligands\(^{36,39}\).

The other bands around 27500 cm\(^{-1}\) may be assigned to \(\pi \rightarrow \pi^*\) transition localised in the coupled azomethine chromophore and the band around 37800 cm\(^{-1}\) to \(\pi \rightarrow \pi^*\) transition of the phenolic group in the ligand\(^{30}\). Thus, the spectra of PH and APH complexes can best be interpreted in terms of tetragonal (\(D_{4h}\)) symmetry while those of INH and AH complexes can be interpreted in terms of square-pyramidal (\(C_{4v}\)) symmetry. The energies of various orbitals can be calculated using equations:

\[6D_q-2D_S-6D_t(\delta_2)\ (\varepsilon^2), \ 6D_q+2D_S-D_t(\delta_2)\ (\delta_{2x-y_2}), \ -4D_q-D_S+4D_t(\varepsilon)\ (\delta_{2z}), \ -4D_q+2D_t-D_t(\delta_2)\ (\delta_{xy}).\]

Thus, it is possible to make some useful deductions from the observed spectra and various values of ligand field parameters \(D_q, D_s\) and \(D_t\) can be determined. In the case of tetragonal complexes, the energy of the transition \(b_{1g} \rightarrow b_{1g} \ (\delta_{2y} \rightarrow \delta_{2x-y_2})\) is predicted to be equal to \(D_{qxy}\), the field in the \(xy\) plane. It is unaffected by substitution along the \(z\)-axis, and configurational interaction. \(D_s\) is a second order radial integral which has no counterpart in cubic molecules, whilst \(D_t\) is of fourth order and is related to \(D_{qxy}\) and \(D_{qz}\), (in-plane and out-of-plane) ligand fields by the relation \(D_t = 4/\pi (D_{qxy} - D_{qz})\). Therefore, it is possible to calculate the ligand field strength along the \(z\)-axis\(^{84}\). It is interesting to note that in these ligands the in-plane field \(D_{qxy}\) is higher than the out-of-plane field \(D_{qz}\) indicating that the bulky ligand groups occupy in-plane positions while the less bulky groups lie on the \(z\)-axis.

All the complexes studied here belong to \(D_{4h}\) and \(C_{4v}\) symmetries which are comparable. This follows from the argument that the energy levels in a tetragonal complex are determined by the total potential along the \(z\)-axis, regardless of whether this potential is equally or unequally distributed above or below the molecular plane\(^{82}\). In the case of a square-pyramidal field, the potential below or above the plane may be taken as zero. On the basis of these arguments, Lever et al.\(^{36}\) have devised the theory of Normalised Spherical Harmonic Hamiltonian (NSH) to evaluate the absolute ligand field parameters \(D_Q, D_S, D_T, D_{Qz}\) and \(D_{Qy}\). These absolute ligand field parameters are related to the classical
parameters through the equations\textsuperscript{36}:

\[
DS = -7Ds; \quad DT = -\left(\frac{7\sqrt{15}}{2}\right) \cdot Dt
\]

\[
DQ = (6\sqrt{21}) \cdot Dq^4 - \left(\frac{7\sqrt{15}}{2}\right) \cdot Dq^2
\]

The factorisation of the crystal field in tetragonal complexes into equatorial $Dq^4$ and axial $Dq^2$ components can be made in the NSH approach through the equations:

\[
Dq^4 = DQ + (2\sqrt{7}/\sqrt{5}) \cdot DT; \quad \text{and} \quad Dq^2 = DQ - \left(\sqrt{7}/\sqrt{5}\right) \cdot DT
\]

$DQ$ is a measure of the average ligand field experienced by the metal ion unlike the classical $Dq$ which is a measure of the in-plane ligand field. The ratio $DT/DQ$ provides a measure of distortion. The values of NSH parameters have been calculated and are given in Table 2. These values indicate that the six-coordinated complexes are comparatively more distorted than the analogous five-coordinated complexes.

References
10. NAKAMOTO, K., Infrared spectra of inorganic and coordination compounds (J. Wiley and Sons, N.Y.), 1970.