A study of the organic complexes of oxovanadium (IV)

Richard Clement Skevington

Wollongong University College

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"A STUDY OF THE ORGANIC COMPLEXES OF OXOVANADIUM (IV)"

A thesis
submitted in partial
fulfilment of the requirements
for the degree of
Bachelor of Science (Honours)

by

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Mr. F. M. Hall)

Wollongong University College

The University of New South Wales

November, 1968.
## CONTENTS

### SUMMARY

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I - INTRODUCTION</td>
<td></td>
</tr>
<tr>
<td>(a) The Vanadyl (IV) Ion and its Properties (General)</td>
<td>3</td>
</tr>
<tr>
<td>(b) The Electronic Structure of the Vanadyl (IV) Ion</td>
<td>3</td>
</tr>
<tr>
<td>(c) The Stereochemistry of the Complexes</td>
<td>4</td>
</tr>
<tr>
<td>(d) Magnetochemical Properties</td>
<td>5</td>
</tr>
<tr>
<td>(e) The Vanadyl (IV) Ion in Aqueous Solution</td>
<td>5</td>
</tr>
<tr>
<td>(f) The Infra-red Spectrum-The V=O Stretching Frequency</td>
<td>7</td>
</tr>
<tr>
<td>(g) Complexes with Specific Complexing Agents</td>
<td>8</td>
</tr>
<tr>
<td>(h) Biological Significance and Aims</td>
<td>12</td>
</tr>
<tr>
<td>II - EXPERIMENTAL</td>
<td></td>
</tr>
<tr>
<td>(a) pH Titrations of Vanadyl Sulphate</td>
<td>14</td>
</tr>
<tr>
<td>(b) Preparation of the Complexes</td>
<td>18</td>
</tr>
<tr>
<td>(c) Crystallisation of the Complexes</td>
<td>18</td>
</tr>
<tr>
<td>(d) Physical Characteristics of the Vanadyl (IV) Complexes</td>
<td>23</td>
</tr>
<tr>
<td>(e) Crystal Structure</td>
<td>25</td>
</tr>
<tr>
<td>(f) Analyses</td>
<td>26</td>
</tr>
<tr>
<td>(g) Molecular Weights</td>
<td>35</td>
</tr>
<tr>
<td>(h) Magnetic Moments</td>
<td>36</td>
</tr>
<tr>
<td>(i) pK Values</td>
<td>37</td>
</tr>
<tr>
<td>(j) Infra-red Spectra</td>
<td>40</td>
</tr>
<tr>
<td>(k) Melting Points</td>
<td>47</td>
</tr>
<tr>
<td>(l) Continuous Variation Spectroscopy</td>
<td>47</td>
</tr>
<tr>
<td>III - DISCUSSION</td>
<td></td>
</tr>
<tr>
<td>(a) pH Titrations of Vanadyl Sulphate</td>
<td>49</td>
</tr>
<tr>
<td>(b) pH Fall in Titrations of Vanadyl Sulphate</td>
<td>55</td>
</tr>
<tr>
<td>(c) Structure of the Complexes</td>
<td>56</td>
</tr>
<tr>
<td>(d) Molecular Weight</td>
<td>64</td>
</tr>
<tr>
<td>(e) Titrations of Tartrate Complexes</td>
<td>65</td>
</tr>
<tr>
<td>(f) Magnetic Moments</td>
<td>66</td>
</tr>
</tbody>
</table>

### APPENDIX

<table>
<thead>
<tr>
<th>Component</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Computer Programme</td>
<td>67</td>
</tr>
<tr>
<td>&quot;</td>
<td>68</td>
</tr>
<tr>
<td>&quot;</td>
<td>69</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>72</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>76</td>
</tr>
</tbody>
</table>
SUMMARY.

Titrations of solutions of vanadyl sulphate have been carried out with aqueous solutions of:

(a) polyhydroxy alcohols,
(b) phenols,
(c) sodium salts of mono- and di-basic carboxylic acids, and
(d) sodium salts of aliphatic and aromatic carboxylic acids.

Of the titrants used, the following group gave initial falls in pH values:

(a) ortho-dihydroxy benzenes,
(b) sodium salts of aliphatic carboxylic acids which have B-hydroxyl groups,
(c) sodium salts of aromatic acids with both a hydroxyl group and a benzene ring(s) on the \( \alpha \)-carbon (to the carboxyl group).

The above results and the variation in the volume of titrant required to attain the minimum pH value are explained.

Using complexing agents selected on the basis of the anomalous results obtained, twelve vanadyl (IV) complexes, with hydroxy carboxylic acids, the sodium salts of some of them and ortho-hydroxy benzenes were prepared and investigated. The behaviour of these complexes, their magnetic and spectroscopic properties, and their measured molecular weights and pK values have been correlated with structures proposed for four of them. The structures of these four crystalline complexes, prepared by using new solvent systems, are currently being investigated by X-ray diffraction methods.
INTRODUCTION
I - INTRODUCTION.

I (a) The Vanadyl (IV) Ion and its Properties (General):

The oxovanadium (IV) (15) ion, VO$^{2+}$, commonly called the vanadyl ion, has the electronic configuration $[\text{Ar}] 3d^{1}$. A review (17) of vanadyl compounds claims that the vanadyl ion has a discrete existence in compounds and may form stable cationic, anionic or neutral complexes in all three phases. In the solid state (2) and in solution, the ion always occurs co-ordinated to other groups. It has also been stated (17) that the vanadyl ion is "likely to be the most stable biatomic ion known".

I (b) The Electronic Structure of the Vanadyl (IV) Ion:

There is an extensive $\pi$-bond character between the V and the O in the vanadyl ion. In vanadyl complexes (2) the 3d, 4s, 4p metal orbitals are used for bonding with the 2s, 2p$\sigma$, (2pz) and 2p$\pi$ (2px, 2py) orbitals of the vanadyl oxygen and the $\sigma$, $\pi'_1$, $\pi'_2$ group orbitals of the nearest neighbour equatorial ligand atoms as in figure (1).

![Diagram of vanadyl ion structure](image)

**Fig. 1.**—The z-axis, as also the arrows representing the $\pi'_1$ AO's are perpendicular to the plane of the paper. The A's represent the nearest neighbour atom of the ligand, L. Point group is $C_4v$. 
The ligand orbitals used in the hydrated vanadyl ion are the sp-hybrid orbitals of the water oxygen atoms. The hydrated vanadyl ion, $\text{VO(H}_2\text{O)}_\text{5}^{2+}$, is believed to have the four equatorial oxygens equally bound and the axial water more loosely held to the vanadium, as has been considered in terms of the molecular orbital theory by Ballhausen and Gray (2).

I (c) The Stereochemistry of the Complexes:

After considering a wide range of ligands, which all form complexes with an apparent "central 5-co-ordinated vanadium (IV) ion", Jones (II) proposed a tetragonal pyramidal structure, rather than a four or six co-ordinated structure. This (five co-ordinated) structure would have oxygen at the vertex and the V=O as the four-fold axis of symmetry, with the remaining positions of the tetragonal pyramid in a plane, i.e. as the base of the pyramid. It was also suggested (II) that the $d^2sp^2$ or $d^2p^3$ hybridization states of vanadium (IV) would give rise to a pyramidal structure. These hybridization states could then readily be converted to $d^2sp^3$ hybridization with ligands which gave a 6-co-ordinated (octahedral) system. This violation (10) of the rule of constancy of co-ordination number by vanadyl (IV) complexes has been well established. (44) The five-co-ordinate anhydrous bis-acetylacetonato vanadyl (IV) complex $[\text{VO(acac)}_2^+]$ has been studied by x-ray crystallography and has been found to have a square pyramidal structure, in agreement with the proposition (II) made by Jones. The V=O
is perpendicular to the acetylacetonato oxygen base of pyramid, with the vanadium above the plane of the oxygen donor atoms.

I (d) Magnetochemical Properties:

Room temperature magnetic moments of vanadyl (IV) complexes have been found (2) to be approximately equal to the spin-only value of 1.73 BM for paramagnetic ions with one (unpaired)d-electron. This value for the magnetic moment is to be expected when the orbital contribution is completely quenched in a low symmetry field as in vanadyl complexes.

I (e) The Vanadyl (IV) Ion in Aqueous Solution:

In solution, the vanadyl (IV) ion may be present either as $V^{2+}$ (with 5 distantly co-ordinated water molecules) or as $V(OH)_{2}^{2+}$. Ballhausen and Gray (2) suggest that the available spectral and magnetic evidence supports the $V^{2+}$ ion, but does not eliminate the $V(OH)_{2}^{2+}$ as a possible form of the ion. The positions of the ultraviolet and visible absorption maxima found for the $VOSO_{4}5H_{2}O$ crystal are virtually the same as those found for an aqueous vanadyl sulphate solution, showing that no significant structural changes occur in going from the crystal form to solution as expected. Ballhausen and Gray (2) believe formation of $V(OH)_{2}^{2+}$ would involve significant structural changes.
To explain the properties of dilute solutions of the vanadyl ion, two new species were assumed by Rossotti and Rossotti (14). These new species, VOOH\(^+\) and (VO)\(_2\)(OH)\(_2\)\(^{2+}\) were formed according to the equations:

\[
\begin{align*}
V\text{O}^{2+} + H_2O & \rightarrow VOOH^+ + H^+; 10^{-6.0 \pm 0.1} \\
2V\text{O}^{2+} + 2H_2O & \rightarrow (VO)_2(OH)_2^{2+} + 2H^+; 10^{-6.88 \pm 0.04}
\end{align*}
\]

and the dimerisation reaction:

\[
2VOOH^+ \rightarrow (VO)_2(OH)_2^{2+}.
\]

The formation of a vanadyl hydroxide precipitate (14) occurred when approximately 10% of the vanadyl ions were further hydrolysed. These authors noted that in the above dimer, and in the corresponding dimers for UO\(^{2+}\) and Cu\(^{2+}\), the M(OH)\(_2\) 'link' of the polynuclear species

\[
(VO)_2(OH)_2^{2+} = VO[VO(OH)_2]^{2+}
\]

is uncharged and the metal hydroxyl ion ratio is the same as in the precipitate.

Rossotti & Rossotti (14) also claim the vanadyl ion "showed no tendency to combine with protons even at the highest acidity studied", viz. 2.5M.H\(^+\). This resistance to protonation has been explained in terms of the molecular orbital bonding scheme (2). The oxygen 2p orbitals are used for \(\pi\)-bonding; only the non-bonding sp\(_d\) hybrid orbital is left for the proton, but it has considerable 2s character and is energetically unsuited for bonding purposes (2).

However, Swift and co-workers (16) have suggested protonation of aquated vanadyl ions does take place, and have
proposed:

\[ \text{VO}(\text{H}_2\text{O})_5^{2+} + \text{H}_3\text{O}^+ \rightarrow \text{encounter complex (EC)} \]  

\[ \text{EC} \xrightarrow{k_a} \text{hydrogen-bonded complex (HBC)} \]  

\[ \text{HBC} \xrightarrow{k_b} \text{VO}(\text{H}_2\text{O})_5^+ + \text{H}_2\text{O} \]  

as a mechanism, with substep (2) as the rate determining step.

I (f) The Infra-red Spectrum - The V=O Stretching Frequency:

Infra-red spectra support VO\(^{2+}\) as the form of the vanadyl (IV) ion (4).

The environment of the vanadyl ion has a marked effect upon the stretching frequency of the V=O double bond. The co-ordination of ligands which donate sigma electron pairs will increase the electron density in metal d-orbitals and as a result decrease \(\pi^* - d\pi\) donation from the oxygen to the vanadium and consequently lower the V-O stretching frequency. This may be expected to depend upon the donor and co-ordinating ability of the ligand provided \(\pi\)-bonding is unimportant. If there is meaningful \(\pi\)-bonding due to the ligand then there will be still further weakening of V-O double bond.
Complexes with Specific Complexing Agents.

Numerous complexes of the vanadyl (IV) ion with various ligands have been prepared and studied; of these the recorded properties of the tartrate, citrate, malonate, maleate, oxalate, catechol and pyrogallol complexes are important to this topic.

Oxalates, Malonates and Maleates of the Vanadyl Ion.

The five co-ordinate \( \text{VO} \text{Ox}_2 \text{H}_2 \text{O} \) has a tetragonal pyramidal structure \((29)\), whilst the tetrahydrate has the same structure with the other two water molecules in the crystal lattice. The corresponding tri-hydrate \( \text{VO} \text{Ox}_3 \text{H}_2 \text{O} \) \((42)\) has been prepared. In solution, the five co-ordinate (square pyramidal) molecules, \( \text{VO} \text{Ox}_2 \text{H}_2 \text{O} \), take up a solvent molecule at a much longer distance in the vacant position trans-to the oxygen of the \( \text{V=O} \) bond of the vanadyl (IV) ion, completing the distorted octahedral arrangement with roughly \( C_{4v} \) symmetry \((29, 30, 31, 32)\).

Oxalate complexes with the acid half neutralised have been reported. The existence of \( \text{V} \text{O(Hox)}_2 \) was demonstrated by Zolotavin and Kalugina \((36)\) who also suggested the possible formation of \( \text{V} \text{O(Hox)}^+ \), but found no evidence for the formation of the anion \( \text{V} \text{O(OH)ox}^- \). However, in conflict with the above work, Ducret \((34)\) claims to have found evidence for the existence of \( \text{V} \text{O(OH)ox}^- \). He also found that the complex \( (\text{V} \text{Oox}_2)^2^- \) was stable in acid solution, while \( [\text{V} \text{Oox}]^- \) was only formed when
the oxalate concentration was large compared to that of the vanadyl (IV) ion.

Vanadyl malonate and maleate complexes (31) have similar properties to the corresponding oxalato-complexes (31).

Oxalate complexes of the form $M_2(VO)_{2}Ox_3 \times H_2O$ were prepared by Sathyanarayana and Patel (30), who found V-V and V-O-V-O types of bonding were absent and suggested that the VO groups were separated by oxalate ions. Magnetic moment measurements showed practically no interaction of unpaired electrons of the $[(VO)_{2}]$ groups in the above complexes. In the complex $M_2(VOx_2) \times 2H_2O$, the $(VOx)_2^-$ can have a rectangular pyramidal structure with vanadium above the plane of the oxygen donor atoms which form the base of the pyramid.

**Vanadyl Citrates.**

Spectrophotometric studies (24, 25) have shown the formation of the very stable complex ion $(VOCit)^{2-}$ and possibly of the $[(VO)_2Cit]$ complex. (The four citric acid hydrogens are neutralised by pH 8 in presence of vanadyl sulphate.) The complex $(VO Cit)^{2-}$ is neutralised at the same time as the acidic functional groups of citric acid. This complex, $(VO Cit)^{2-}$, is more stable than the oxalate but less stable than the tartrate complex.
Vanadyl Tartrates

Meso- and D-(-)-tartaric acids are stereoisomers (40):

\begin{align*}
&\text{Mesotartaric acid} \\
&\text{d-(-)-Tartaric acid}
\end{align*}

Figure 2.

Meso-tartaric acid has a plane of symmetry and is optically inactive. D-(-)-tartaric acid has no plane of symmetry and is optically active.

Tartaric acid is a potential quadridentate ligand (7, 17, 18, 26). All the tartrate complexes prepared to date have $\text{VO : ligand = 1:1 (7, 17, 18, 24)}$ and the following empirical formulae have been suggested:

\begin{align*}
&\text{VO (D-tartaric acid) } 1\text{H}_2\text{O} \\
&\text{VO Na}_2 \text{ (D-tartrate) } 1\text{H}_2\text{O} \\
&\text{VO (meso-tartaric acid) } 1\text{ or } 2\text{H}_2\text{O}
\end{align*}

The high water solubility of the tartrate complexes suggests that the complexes are charged (7).

In their work on vanadyl tartrates, Gellert and Hall (7)
found that the magnetic moments for the complexes were all approximately equal to the spin-only value of 1.73 B.M. which is the value for a one electron paramagnetic ion. This is in agreement with earlier work (2).

Vanadyl Polyhydroxybenzenes.

Polyhydroxybenzenes (PH₂) (17) form (VO (P)) complexes in the pH range 4 - 5, whereas at higher pH values [VO(P)₂]^{2-} type complexes are formed.

Catechol Complexes of the Vanadyl Ion.

Potentiometric titrations (12) of vanadyl sulphate in alkaline conditions have shown the feasibility of 1 : 1 and 1 : 2 VO : catechol complexes. Above pH 4 the 1 : 1 complex hydrolyses

\[
\text{VOA} + \text{H}_2\text{O} \rightarrow \text{VO(OH)}\text{A}^- + \text{H}^+.
\]

Continuous variation studies (21) showed a violet 1 : 2 complex and a violet-black 1 : 3 catechol complex were formed.

The compounds all seem to contain "catechol of crystallisation" as well as water of crystallisation (17).

The vanadyl (IV) also forms:

\[
\begin{align*}
&\left[\text{VO (C}_6\text{H}_{(6-n)}\text{(OH)}_{n-1})_0\right]^+ \\
&\left[\text{VO (C}_6\text{H}_{(6-n)}\text{(OH)}_{n-2}O_2\right]_2^{2-}
\end{align*}
\]

complexes at pH 3 and pH 5 - 8 respectively (27, 28, 34).
I (h) Biological Significance and Aims.

One of the reasons for the interest in vanadyl complexes is their possible biological significance especially in the fields of:

(1) the possible inhibition of cholesterol synthesis in brain tumours by \( (\text{NH}_4)_2 \text{VO(tartrate)} \cdot \text{H}_2\text{O} \) (23);

and

(11) blood pressure reducing agents. Work in this field has been limited by the absence of a complexing agent which would eliminate the reported toxic effects of the vanadium or vanadyl ions. As the complexes being studied could possibly release vanadium ions slowly, the level of their concentration could be regulated over a long period of time.

This project was intended to prepare a series of vanadyl (IV) complexes in pure crystalline form, to investigate the reported anomalous properties of some of these complexes and to correlate the results obtained with their structure.
II - EXPERIMENTAL.
II - EXPERIMENTAL.

The experimental methods used and the quantitative results obtained will be presented in this section. Where they are available, the experimental results of other workers will be given to enable comparisons to be made.

II (a) **pH Titration of vanadyl sulphate.**

Fifty mls of an aqueous solution containing $10^{-3}$ moles of vanadyl sulphate were titrated with 0.1 M aqueous solutions of certain alcohols, phenols and salts of carboxylic acids. An expanded scale Radiometer type TTT1 Fig. 3 was used for determining the pH. A 10 ml addition of titrant corresponds to a 1:1 mole ratio of ligand to vanadyl ion.

All the sodium hydroxycarboxylates used gave an initial pH drop with the exception of the coumarate, p-hydroxy benzoate, glycollate and lactate, (Structures - Tables 1 & 2, Titration curves - Figures 4 & 5). Also no carboxylates or alcohols caused a pH drop, (Tables 3 & 4, Figures 6 & 7).

Catechol and pyrogallol were the only phenols which gave pH minima in the titrations, (Table 4, Figure 7).

Problems associated with these titrations were:

1) the titrations may reach equilibrium only slowly.
2) the cell was not thermostated, so that small pH changes with temperature may have occurred.
3) No provision was made against aerial oxidation of vanadyl ions at higher pH values (19).
Footnotes:

(The addition of 0.1M NaOH to vanadyl sulphate solution gave a rapid increase in pH. Freshly prepared blue vanadyl sulphate solution slowly turns green with time, finally giving rise to a precipitate and a drop in pH.)

Table 5 lists the titrants, the volume of titrant required to obtain the pH minimum, and the maximum fall in pH recorded. Also shown in the table are the corresponding results previously obtained by Gellert and Hall (7).
Figure 3.

pH Meter.
STRUCTURES: HYDROXY CARBOXYLIC ACIDS.

\[ \text{a-tartaric acid} \]

\[ \text{salicylic acid} \]

\[ \text{benzilic acid} \]

\[ \text{glycollic acid} \]

\[ \text{malic acid} \]

\[ \text{lactic acid} \]


**STRUCTURES OF HYDROXY CARBOXYLIC ACIDS.**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>gluconic acid</td>
<td>C₅H₆(OH)₅COOH</td>
</tr>
<tr>
<td>mandelic acid</td>
<td><img src="image" alt="Mandelic Acid Structure" /></td>
</tr>
<tr>
<td>mucic acid</td>
<td>((\text{CHOH})₄\text{COOH})</td>
</tr>
<tr>
<td>meso-tartaric acid</td>
<td>(\text{HO} - \text{C} - \text{COOH})</td>
</tr>
<tr>
<td>(p)-hydroxy benzoic acid</td>
<td>(\text{HO} - \text{O} - \text{COOH})</td>
</tr>
<tr>
<td>citric acid</td>
<td><img src="image" alt="Citric Acid Structure" /></td>
</tr>
</tbody>
</table>
1. Gluconate $\text{C}_5\text{H}_6(\text{OH})_5\text{COOH}$
2. Mandelate $\text{C}_6\text{H}_5\text{CH(OH)COOH}$
3. Mucate $\text{HOOC(CHOH)}_4\text{COOH}$
4. Meso-tartrate $(\text{CH(OH)COOH})_2$ $d$
5. p-Hydroxy-benzoate $\text{HOOC}_6\text{H}_4\text{COOH}$
6. Coumarate (hydroxy-cinnamate)
7. Citrate

Figure 4

mls of 0.1M Titrant
SODIUM HYDROXY-CARBOXYLATES

1. D-tartrate $\text{HOOC(CHOH)}_2\text{COOH}$
2. Salicylate $C_6H_4(\text{OH})\text{COOH}$
3. Benzilic $(C_6H_5)_2C(\text{OH})\text{COOH}$
4. Glycollate $\text{CH}_2(\text{OH})\text{COOH}$
5. Malate $\text{HOOCCH}_2\text{CHOHCOOH}$
6. Lactate $\text{CH}_3\text{CH(\text{OH})COOH}$

Figure 5
SODIUM CARBOXYLATES

1. Adipate $\text{HOOC}(\text{CH}_2)_4\text{COOH}$
2. Malonate $\text{CH}_2(\text{COOH})_2$
3. Succinate $(\text{CH}_2\text{COOH})_2$
4. Oxalate $(\text{COOH})_2$
5. Phthalate $\text{C}_6\text{H}_4(\text{COOH})_2$
6. Cinnamate $\text{C}_6\text{H}_5\text{CH}=$CHCOOH

Figure 6

mls of 0.1 M titrant
ALCOHOLS.

TABLE 4.

ALCOHOL

 STRUCTURE.

resorcinol

\[
\begin{array}{c}
\text{O} \\
\text{H}
\end{array}
\]

catechol

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{H}
\end{array}
\]

pyrogallool

\[
\begin{array}{c}
\text{O} \\
\text{H} \\
\text{H} \\
\text{H}
\end{array}
\]

glycol

\[
\begin{array}{c}
\text{C} \\
\text{H}_2 \\
\text{O} \\
\text{H}
\end{array}
\]

phenol

\[
\begin{array}{c}
\text{O}
\end{array}
\]

mannitol

\[
\begin{array}{c}
\text{C} \\
\text{H}_2 \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{C} \\
\text{H}_2 \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{C} \\
\text{H}_2 \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{C} \\
\text{H}_2 \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{C} \\
\text{H}_2 \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{C} \\
\text{H}_2 \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{C} \\
\text{H}_2 \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{C} \\
\text{H}_2 \\
\text{O} \\
\text{H}
\end{array}
\]

\[
\begin{array}{c}
\text{C} \\
\text{H}_2 \\
\text{O} \\
\text{H}
\end{array}
\]
ALCOHOLS AND PHENOLS

Figure 7

1. Resorcinol 1,3 dihydroxy-benzene
2. Catechol 1,2 dihydroxy-benzene
3. Pyrogallol 1,2,3 trihydroxy-benzene
4. Glycol \((\text{CH}_2\text{OH})_2\)
5. Phenol \(\text{C}_6\text{H}_5\text{OH}\)
6. Mannitol \(\text{CH}_2\text{OH}[(\text{CHOH})_4\text{CH}_2\text{OH}\]

\[\text{pH} \]
<table>
<thead>
<tr>
<th>Complexing Agent</th>
<th>Volume to attain pH minimum</th>
<th>Maximum fall in pH units</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>present work</td>
<td>previous work</td>
</tr>
<tr>
<td>Tri-sodium citrate</td>
<td>4 mls.</td>
<td>5 mls.</td>
</tr>
<tr>
<td>Sodium D-tartrate</td>
<td>7 &quot;</td>
<td>6.5 &quot;</td>
</tr>
<tr>
<td>Sodium meso-tartrate</td>
<td>4 &quot;</td>
<td>4 &quot;</td>
</tr>
<tr>
<td>Sodium malate</td>
<td>2.5&quot;</td>
<td>3 &quot;</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>7 &quot;</td>
<td>5 &quot;</td>
</tr>
<tr>
<td>Sodium mucate</td>
<td>3 &quot;</td>
<td>3 &quot;</td>
</tr>
<tr>
<td>Sodium benzilate</td>
<td>6.5&quot;</td>
<td>10 &quot;</td>
</tr>
<tr>
<td>Sodium mandelate</td>
<td>7 &quot;</td>
<td>7 &quot;</td>
</tr>
<tr>
<td>Sodium salicylate</td>
<td>6 &quot;</td>
<td>7 &quot;</td>
</tr>
<tr>
<td>Gallocate</td>
<td>60 &quot;</td>
<td>27 &quot;</td>
</tr>
<tr>
<td>Pyrogallol</td>
<td>41 &quot;</td>
<td>29 &quot;</td>
</tr>
</tbody>
</table>
II (b) Preparation of the Complexes:

All the complexes were prepared by the following method (7):
vanadyl hydroxide was precipitated by the addition of dilute
sodium hydroxide to an aqueous solution of vanadyl sulphate
until the solution had a pH between pH 5.6 & 6. This pH was
chosen so as to minimise the oxidation of vanadyl (IV) to
vanadium (V)(5, 19), and not to allow the precipitate to
dissolve in any excess hydroxide (3). The grey-brown hydroxide
was separated and washed using a centrifuge. (Britton & Welford,
(3) claimed that a precipitate of composition VO(OH)₂ is formed
on addition of alkali to vanadyl sulphate.) Slightly less than
an equimolar quantity of ligand was dissolved in water and added
to the suspension of vanadyl hydroxide in water. After the
mixture had been digested on a boiling water bath, the excess
vanadyl hydroxide was filtered off and the solution evaporated.

II (c) Crystallisation of the Complexes:

Crystallisation of the complexes prepared was attempted for
two reasons:
(a) to obtain crystals which may be studied by X-ray crystallography; and
(b) to purify the complexes.

The following complexes were prepared by the above method:
vanadyl complexes of meso- and D-tartaric acids, citric acid, the
sodium salts of the above acids, lactic acid, catechol, malic acid,
pyrogallol, gluconic acid, mucic acid, salicylic acid and mandelic acid. Of these only four could be crystallised, viz. vanadyl, D- and meso-tartrates, vanadyl sodium D-tartrate and vanadyl sodium citrate. (The vanadyl citric acid complex could not be crystallised despite the wide range of solvents, conditions and solvent mixtures used. Attempts to crystallise the sodium meso-tartrate complex from water resulted in destruction of the complex.)

Factors affecting the crystallisation include:

(1) **Concentration Dependence:**
With the addition of a non-solvent (4l) to an aqueous solution of the complex no change took place if ---

(a) insufficient of the non-solvent was added;

or (b) the aqueous solution was too dilute when the non-solvent was added. (The latter problem could sometimes be overcome by the addition of a large excess of the non-solvent; but this gave poor yields and was poor chemical technique.);

or (c) The complex came out of solution as an oil or precipitate if too much of the non-solvent was added.

(2) **Oxidation:**
The vanadyl ion may be oxidised to vanadium (V) in aqueous solution, especially at higher pH values. To avoid this crystallisations were carried out under nitrogen.

(3) **Yield:**
The crystallisations frequently gave low yields which could have been due to:
(a) the requirement that the conditions for recrystallisation be as mild as possible to minimise the co-precipitation of the impurities with the complex.

(b) impurities, probably oxidation products, for example:

(I) in the recrystallisation of mauve vanadyl sodium D-tartrate the mother liquor after recrystallisation was green-brown; after each recrystallisation, the mother liquor was less discoloured.

(II) a black compound was separated from the blue tri-sodium citrate complex.

(4) Solvent for Washing:

The very high solubility of the complexes even in cold water prohibited the use of this solvent to wash the crystals.

Generally, both complexes and impurities were insoluble in most other solvents; the use of solvents in which the complex (and impurities) were insoluble caused the ions remaining in the mother liquor about the crystals to precipitate out on the filter or to form oil around the crystals. Mixed solvents were not practical, as the correct solvent ratio was not known, so that the crystals would either dissolve, if the solvent mixture contained too much water, or become contaminated, if the solvent mixture contained too little water (i.e. too much non-solvent).
Crystallisation Techniques.

The following crystallisation techniques were used:

The vanadyl D-tartrate complex was crystallised (7) by adding sufficient of the "non-solvent" (41) dioxane, so that the complex would crystallise out of a hot concentrated aqueous solution on cooling. Peroxides had to be removed from the dioxane before it was used in the crystallisation, to prevent the peroxides oxidising the vanadyl ions to vanadium (v). The crystallisation had to be carried out in an inert atmosphere (i.e. under nitrogen) to prevent further peroxide formation.

Vanadyl Sodium D-tartrate: two methods were successfully used to crystallise this complex, viz:

(a) The addition of a non-solvent to an aqueous solution. Sufficient n-propanol was added to a hot concentrated aqueous solution of the complex so that crystallisation would occur when the solution was cooled. Normally, crystallisations involving the addition of a non-solvent to a solution of the complex have a turbidity at the critical solvent concentration required for crystallisation. The addition of n-propanol to an aqueous solution of the vanadyl sodium D-tartrate does not give a turbid solution at the critical solvent ratio. An excess of the non-solvent, n-propanol, was indicated by the presence of a clear upper (second) layer. This excess of non-solvent caused the complex to settle out of solution as an oil. The addition of water, just sufficient to give a homogeneous mixture after shaking, would give a solution from which crystallisation would occur on cooling.
(b) **Crystallisation from an aqueous solution:**

Crystals formed when an aqueous solution of the complex was evaporated to a very small volume.

Method (a) has the advantage that the volume from which crystallisation occurs is large so that co-precipitation of impurities is less likely than in method (b). However, the former method has the disadvantage that, on cooling, the solvent may form two layers with different solvent ratios in each. This means that if crystallisation has not occurred by the time these layers have formed, then the crystals form or grow in different solvent media, with the possibility that different species will form from each layer.

The single solvent method has the advantage that there is no possibility of the introduction of impurities with the non-solvent or that the non-solvent will form part of the crystal. But the small volume means that co-precipitation of impurities is likely to occur.

Both methods of crystallisation required several recrystallisations to obtain pure crystals.

The **vanadyl sodium citrate** prepared by the method given earlier (p,18) was a black powdery solid. Addition of ethanol to a hot aqueous solution of this compound caused a black oil to settle leaving a blue solution. The solution was decanted and concentrated (by evaporation). Sufficient ethanol to just salt out the black compound was again added. This process was repeated till no more black compound could be salted out of the solution. Then a
<table>
<thead>
<tr>
<th>Complexing Agent</th>
<th>Appearance</th>
<th>Appearance when dried over P$_2$O$_5$ at 100°c.</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-tartaric acid</td>
<td>dark blue solid forms blue crystals</td>
<td>dark blue solid or crystals</td>
</tr>
<tr>
<td>sodium D-tartrate</td>
<td>mauve-purple crystals</td>
<td>pale mauve crystals</td>
</tr>
<tr>
<td>meso-tartaric acid</td>
<td>dark blue solid blue crystals</td>
<td>dark blue solid</td>
</tr>
<tr>
<td>citric acid</td>
<td>blue solid</td>
<td>dark green compound</td>
</tr>
<tr>
<td>tri-sodium citrate</td>
<td>black powdery solid when prepared crystallises into blue crystal needles</td>
<td>pale blue</td>
</tr>
<tr>
<td>Malic acid</td>
<td>Blue-grey powder</td>
<td></td>
</tr>
<tr>
<td>Lactic acid</td>
<td>grey powder</td>
<td></td>
</tr>
<tr>
<td>gluconic acid</td>
<td>blue-grey powder</td>
<td></td>
</tr>
<tr>
<td>pyrogallol</td>
<td>black powder</td>
<td></td>
</tr>
<tr>
<td>salicylic acid</td>
<td>&quot; &quot;</td>
<td></td>
</tr>
<tr>
<td>mandelic acid</td>
<td>grey powder</td>
<td></td>
</tr>
</tbody>
</table>
slightly higher proportion of ethanol was added to a hot concentrated aqueous solution of the complex. Clusters of blue crystal needles formed on cooling. (If less ethanol was used in the first step then, on cooling, black crystals and blue crystals formed. The blue crystals formed from the impure solution appeared to be rectangular cuboid in shape.)

II (d) Physical Characteristics of the Vanadyl (IV) Complexes.

(I) Appearance.

Most of the vanadyl complexes prepared were blue. The ligands and the colours of the complexes prepared are given in Table 6. (Page 23.)

(II) Solubilities.

The solubilities of certain vanadyl complexes in a wide range of solvents was tested. The complexes were found to be insoluble in most organic solvents. The results are tabulated in Table 7:

<table>
<thead>
<tr>
<th>Complexing Agent</th>
<th>Solvents in which the complex is:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>soluble hot and cold</td>
</tr>
<tr>
<td>D-tartaric acid</td>
<td>water</td>
</tr>
<tr>
<td>Sodium D-tartrate</td>
<td>&quot;</td>
</tr>
<tr>
<td>Citric acid</td>
<td>&quot;</td>
</tr>
<tr>
<td>Tri-sodium citrate</td>
<td>&quot;</td>
</tr>
<tr>
<td>Salicylic acid</td>
<td>soluble in hot water</td>
</tr>
<tr>
<td>Mucic acid</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

The complexes were often soluble in mixtures of organic solvents with water, but this may merely have been due to the solubility in the water of the mixtures.
II (e) **Crystal Structure.**

The crystals prepared had physical characteristics:

**Vanadyl Sodium D-tartrate.**

(I) Recrystallised from water and n-propanol.  
The complex formed small square pyramidal crystals. They were purple in colour.

(II) Recrystallised from water.  
These crystals were rectangular cuboid in shape and generally larger than those formed in method (I). Again the crystals were purple, but not quite as deep in colour.

**Vanadyl D-tartrate.**

The complex crystallised as plate crystals, navy blue in colour.

**Vanadyl Sodium Citrate.**

The fine crystal needles were light blue in colour.

**Vanadyl meso-tartrate.**

Blue crystal needles were formed.
Analyses.

Analyses for vanadium, sodium, carbon, hydrogen and volatiles were carried out upon the complexes prepared. Oxygen could not be determined as metal-containing compounds damage the combustion tube in the determination.

Vanadium was determined by fuming the complex with a mixture of 2:1 concentrated nitric and sulphuric acids to destroy the organic matter, then dissolving the residue in 2 - 5% sulphuric acid solution. Sulphur dioxide was passed through the boiling solution to reduce the vanadium to the vanadyl ion, then the volume of the solution was reduced by boiling.

The solution was diluted with water and the hot solution titrated with standardised potassium permanganate. The equation for the reaction is:

\[ \text{MnO}_4^- + 8 \text{H}^+ + 5 \text{V}^{1+} \rightarrow \text{Mn}^{2+} + 4 \text{H}_2\text{O} + 5 \text{V}^\text{V} \]

The determination may be repeated by carrying out the above process from the reduction step.

Sodium was determined by atomic absorption spectrophotometric methods.

Carbon and hydrogen analyses were done by conventional methods.

Water and volatile determination was carried out by placing a known weight of the sample in a drying pistol. This was then heated to 100°C under reduced pressure. Phosphorus pentoxide was used to absorb the water and volatile compounds released.

Table 8 gives the analyses obtained for the complexes by the above methods and the conditions under which the complexes were prepared. Analyses obtained by other workers and for possible
theoretical formulae are also given.

The complexes were initially dried over calcium chloride at room temperature and atmospheric pressure. Further drying was carried out by the method described above.

The loss in weight on subjecting the complex to the vigorous drying procedure mentioned is given in the column headed volatiles.

<table>
<thead>
<tr>
<th>TABLE 8.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vanadyl meso-tartrate</td>
</tr>
<tr>
<td>% V</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>20.3</td>
</tr>
<tr>
<td>19.6</td>
</tr>
</tbody>
</table>

Calc. for VO(C₄O₆H₄)₂H₂O

B | 28.4 | 16.2 | 2.7 | compound A dried over P₂O₅ at 100°C. |

C | 22.1 | 19.5 | 2.6 | ref. 7 dried at 110°C. |

Since compound A was not crystalline and was hygroscopic, then while it was awaiting carbon and hydrogen analyses, it probably absorbed water. This could help explain the poor correlation of found and calculated percentages.
# Table 8 (contd.)

<table>
<thead>
<tr>
<th></th>
<th>% V</th>
<th>% C</th>
<th>% H</th>
<th>% volatile</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td>25.2</td>
<td>17.8</td>
<td>2.8</td>
<td>unrecrystallised dried over CaCl&lt;sub&gt;2&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td><strong>B</strong></td>
<td>20.8</td>
<td>19.2</td>
<td>1.6</td>
<td>calc. for VO(C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;)</td>
<td></td>
</tr>
<tr>
<td><strong>C</strong></td>
<td>19.1</td>
<td>17.9</td>
<td>3.7</td>
<td>&quot;</td>
<td>3H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td><strong>D</strong></td>
<td>20.1</td>
<td>17.7</td>
<td>3.7</td>
<td>ref. 7</td>
<td></td>
</tr>
<tr>
<td><strong>E</strong></td>
<td>16.6</td>
<td>27.5</td>
<td>5.2</td>
<td>30.4</td>
<td>crystallise from water and dioxane.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>29.4*</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td><strong>F</strong></td>
<td>16.2</td>
<td>27.9</td>
<td>4.3</td>
<td>30</td>
<td>calc. for (VO)&lt;sub&gt;6&lt;/sub&gt;(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;)&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;5&lt;/sub&gt;9H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td><strong>G</strong></td>
<td>22.6</td>
<td>21.8</td>
<td>4.0</td>
<td>compound E dried over P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td><strong>H</strong></td>
<td>23.3</td>
<td>21.9</td>
<td>1.9</td>
<td>calc. for VO(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22.8</td>
<td>21.4</td>
<td>2.2</td>
<td>&quot;</td>
<td>0.5H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td><strong>I</strong></td>
<td>13.9</td>
<td>17.9</td>
<td>2.9</td>
<td>E dissolved in water and the solvent evaporated.</td>
<td></td>
</tr>
<tr>
<td><strong>J</strong></td>
<td>14.0</td>
<td>26.2</td>
<td>5.5</td>
<td>E recrystallised from H&lt;sub&gt;2&lt;/sub&gt;O &amp; dioxane</td>
<td></td>
</tr>
<tr>
<td><strong>K</strong></td>
<td>15.5</td>
<td>28.0</td>
<td>4.9</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td><strong>L</strong></td>
<td>15.1</td>
<td>28.4</td>
<td>4.7</td>
<td>calc. for VO(C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;6&lt;/sub&gt;)(C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
</tbody>
</table>

The volatile in the formula was dioxane and water.

Compound A has VO: tartrate = 6:5.

The uncrystallised and "dried" compounds absorb water; this may help to explain the (above) VO:tartrate ratio of 6:5.
<table>
<thead>
<tr>
<th>Compounds</th>
<th>% V</th>
<th>% Na</th>
<th>% C</th>
<th>% H</th>
<th>% H₂O</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>15.5</td>
<td>14.4</td>
<td>14.8</td>
<td>2.6</td>
<td></td>
<td>uncrystallised</td>
</tr>
<tr>
<td>B</td>
<td>15.4</td>
<td>13.9</td>
<td>14.6</td>
<td>3.0</td>
<td></td>
<td>calc. for VO\textsubscript{2}Na\textsubscript{2}(C\textsubscript{4}H\textsubscript{2}O\textsubscript{6})\textsubscript{4}H\textsubscript{2}O</td>
</tr>
<tr>
<td>C</td>
<td>18.8</td>
<td>15.6</td>
<td>15.7</td>
<td>2.5</td>
<td></td>
<td>A dried over P\textsubscript{2}O\textsubscript{5}, 100\degree C.</td>
</tr>
<tr>
<td>D</td>
<td>18.2</td>
<td></td>
<td>16.4</td>
<td>2.3</td>
<td></td>
<td>Ref.7 dried at 110\degree C.</td>
</tr>
<tr>
<td>E</td>
<td>16.9</td>
<td>11.7</td>
<td>14.1</td>
<td>2.7</td>
<td>18.4</td>
<td>crystalised from water and n-propanol</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>18.9 *</td>
</tr>
<tr>
<td>F</td>
<td>17.0</td>
<td>11.4</td>
<td>16.2</td>
<td>2.8</td>
<td></td>
<td>calc. for (VO)\textsubscript{2}Na\textsubscript{3}(C\textsubscript{4}H\textsubscript{2}O\textsubscript{6})\textsubscript{6}H\textsubscript{2}O</td>
</tr>
<tr>
<td></td>
<td>16.4</td>
<td>11.2</td>
<td>15.4</td>
<td>3.1</td>
<td>20.2</td>
<td>&quot; &quot; &quot; &quot; &quot; &quot; &quot; 7 &quot; &quot; &quot; &quot; &quot; &quot; 9 &quot;</td>
</tr>
<tr>
<td></td>
<td>15.5</td>
<td>10.7</td>
<td>14.8</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>20.2</td>
<td>13.9</td>
<td>15.5</td>
<td>2.6</td>
<td></td>
<td>E dried over P\textsubscript{2}O\textsubscript{5}, 100\degree C.</td>
</tr>
<tr>
<td>H</td>
<td>16.8</td>
<td>13.9</td>
<td>15.4</td>
<td>2.8</td>
<td>17.5</td>
<td>crystalised from water &amp; n-propanol with a little dilute NaOH added to the solution</td>
</tr>
<tr>
<td>I</td>
<td>16.3</td>
<td>14.7</td>
<td>15.3</td>
<td>2.6</td>
<td>17.4</td>
<td>calc. for VO\textsubscript{2}Na\textsubscript{2}(C\textsubscript{4}H\textsubscript{2}O\textsubscript{6})\textsubscript{3}H\textsubscript{2}O</td>
</tr>
<tr>
<td>J</td>
<td>20.2</td>
<td>16.4</td>
<td>15.7</td>
<td>2.8</td>
<td></td>
<td>H dried over P\textsubscript{2}O\textsubscript{5}, 100\degree C.</td>
</tr>
<tr>
<td>K</td>
<td>16.7</td>
<td>13.4</td>
<td>15.4</td>
<td>2.7</td>
<td></td>
<td>crystalised from water with a little dilute NaOH solution added</td>
</tr>
<tr>
<td>L</td>
<td>16.3</td>
<td>13.7</td>
<td>15.3</td>
<td>2.6</td>
<td></td>
<td>calc. for VO\textsubscript{2}Na\textsubscript{2}(C\textsubscript{4}H\textsubscript{2}O\textsubscript{6})\textsubscript{3}H\textsubscript{2}O</td>
</tr>
</tbody>
</table>

Experimental results in % H₂O column for compound E & H may also contain n-propanol in the figures given.

Compounds dried over P₂O₅, 100°C. absorb atmospheric water.

Compound B was uncrystallised.

Attempts to fit n-propanol into analyses for compounds E, G & H were unsuccessful.
### TABLE 8. (contd.)

<table>
<thead>
<tr>
<th></th>
<th>% V</th>
<th>% Na</th>
<th>% C</th>
<th>% H</th>
<th>% H₂O</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>39.8</td>
<td>9.3</td>
<td>1.5</td>
<td>2.2</td>
<td></td>
<td>residue uncrystallised (black)</td>
</tr>
<tr>
<td>B</td>
<td>38.2</td>
<td>7.6</td>
<td>1.9</td>
<td>3.5</td>
<td></td>
<td>A crystallised</td>
</tr>
<tr>
<td>C</td>
<td>11.3</td>
<td>15.9</td>
<td>20.5</td>
<td>2.5</td>
<td>8.3</td>
<td>blue complex—uncrystallised</td>
</tr>
<tr>
<td>D</td>
<td>12.0</td>
<td>18.0</td>
<td>21.7</td>
<td>2.3</td>
<td></td>
<td>C dried over P₂O₅, 100°C.</td>
</tr>
<tr>
<td>E</td>
<td>13.6</td>
<td>9.6</td>
<td>17.0</td>
<td>3.7</td>
<td>25.6</td>
<td>blue complex crystallised from water &amp; ethanol</td>
</tr>
<tr>
<td>F</td>
<td>11.9</td>
<td>10.8</td>
<td>16.8</td>
<td>4.4</td>
<td>29.4</td>
<td>calc. for VO₂Na₂(C₆H₄O₇)·7H₂O</td>
</tr>
<tr>
<td>G</td>
<td>16.4</td>
<td>12.8</td>
<td>20.7</td>
<td>3.2</td>
<td></td>
<td>E dried over P₂O₅</td>
</tr>
<tr>
<td>H</td>
<td>15.2</td>
<td>12.3</td>
<td>20.8</td>
<td>2.8</td>
<td>9.9</td>
<td>E dissolved in water and evaporated</td>
</tr>
<tr>
<td>I</td>
<td>14.4</td>
<td>12.9</td>
<td>20.3</td>
<td>2.8</td>
<td></td>
<td>calc. for VO₂Na₂(C₆H₄O₇)·3H₂O</td>
</tr>
<tr>
<td>J</td>
<td>14.5</td>
<td>12.1</td>
<td>21.5</td>
<td>2.8</td>
<td>17.4</td>
<td>blue complex crystallised from water and ethanol to which a little dilute NaOH had been added</td>
</tr>
<tr>
<td>K</td>
<td>14.4</td>
<td>12.9</td>
<td>20.3</td>
<td>2.8</td>
<td></td>
<td>calc. for VO₂Na₂(C₆H₄O₇)·3H₂O</td>
</tr>
<tr>
<td>L</td>
<td>16.5</td>
<td>14.1</td>
<td>20.7</td>
<td>2.8</td>
<td></td>
<td>J dried over P₂O₅, 100°C.</td>
</tr>
</tbody>
</table>

Compound F has VO:Na as 2:3 from analytic figures.

Compound C has VO:Na as 1:3 from analytic figures.

The compounds dried over P₂O₅, at 100°C, absorbed water.

Analysis H, together with attempts to fit ethanol into analyses for compounds: E and J (which were unsuccessful), suggest ethanol was not incorporated into the compounds.
TABLE 8.  (contd.)

Vanadyl Citrate

<table>
<thead>
<tr>
<th></th>
<th>% V</th>
<th>% C</th>
<th>% H</th>
<th>% Water</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>22.7</td>
<td>21.6</td>
<td>3.5</td>
<td>11.8</td>
<td>uncrysalised</td>
</tr>
<tr>
<td>A2</td>
<td>14.5</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>22.9</td>
<td>21.5</td>
<td>3.0</td>
<td>13.5</td>
<td>calc. for (VO)₃(C₆H₅O₇)₂ 5H₂O</td>
</tr>
<tr>
<td>C</td>
<td>25.3</td>
<td>21.8</td>
<td>2.9</td>
<td></td>
<td>(A1) dried over P₂O₅, 100°C.</td>
</tr>
<tr>
<td>D</td>
<td>22.0</td>
<td>21.9</td>
<td>2.9</td>
<td></td>
<td>(A2) &quot; &quot; &quot; &quot; &quot;</td>
</tr>
</tbody>
</table>

Catechol Complexes of Vanadium (IV)

<table>
<thead>
<tr>
<th></th>
<th>% V</th>
<th>% C</th>
<th>% H</th>
<th>% H₂O</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>11.6</td>
<td>46.8</td>
<td>4.1</td>
<td>17.5</td>
<td>uncrysalised</td>
</tr>
<tr>
<td>B</td>
<td>11.2</td>
<td>47.2</td>
<td>3.7</td>
<td>13.3</td>
<td>calc. for VO(C₆H₅O₂)₃ 3H₂O</td>
</tr>
<tr>
<td>C</td>
<td>15.0</td>
<td>46.1</td>
<td>3.5</td>
<td></td>
<td>dried over P₂O₅, 100°C.</td>
</tr>
<tr>
<td>D</td>
<td>16.4</td>
<td>46.2</td>
<td>4.2</td>
<td></td>
<td>calc. for VO(C₆H₅O₂)₂ 1.5H₂O</td>
</tr>
<tr>
<td></td>
<td>15.9</td>
<td>44.8</td>
<td>4.4</td>
<td>2</td>
<td>&quot; &quot; &quot; &quot; &quot;</td>
</tr>
<tr>
<td></td>
<td>15.0</td>
<td>42.5</td>
<td>4.7</td>
<td>3</td>
<td>&quot; &quot; &quot; &quot; &quot;</td>
</tr>
</tbody>
</table>

After drying compound A, colourless crystal needles were found in the neck of the drying pistol. These crystals melted in the range 105-107°C. (Catechol melts at 105°C. However, catechol boils at 245°C.) Support for the apparent loss of catechol from compound A could come from the statement that some catechol complexes appear to contain "catechol of crystallisation" (17).
TABLE 8. (cond.)

<table>
<thead>
<tr>
<th>Vanadyl Lactate</th>
<th>% V</th>
<th>% C</th>
<th>% H</th>
<th>% H₂O</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>26.2</td>
<td>20.4</td>
<td>3.8</td>
<td>8.5</td>
<td>Uncrystallised</td>
</tr>
<tr>
<td>B</td>
<td>27.7</td>
<td>20.5</td>
<td>3.9</td>
<td></td>
<td>compound A dried.</td>
</tr>
<tr>
<td>C</td>
<td>21.9</td>
<td>28.0</td>
<td>4.0</td>
<td></td>
<td>ref.7 dried at 110°C.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Vanadyl Malate</th>
<th>% V</th>
<th>% C</th>
<th>% H</th>
<th>% H₂O</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>24.2</td>
<td>19.6</td>
<td>3.1</td>
<td>7.2</td>
<td>uncrytallised</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>9.5*</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>24.2</td>
<td>19.9</td>
<td>2.8</td>
<td>11.7</td>
<td>calc. for (VO)₈(C₄H₅O₅)₇H₂O</td>
</tr>
<tr>
<td>C</td>
<td>23.4</td>
<td>22.0</td>
<td>3.2</td>
<td>16.5</td>
<td>&quot; &quot; VO (C₄H₅O₅) 2H₂O</td>
</tr>
<tr>
<td></td>
<td>23.6</td>
<td>20.3</td>
<td>2.8</td>
<td>22.9</td>
<td>&quot; &quot; &quot; &quot; 3 &quot;</td>
</tr>
<tr>
<td></td>
<td>20.1</td>
<td>18.9</td>
<td>4.3</td>
<td>28.4</td>
<td>&quot; &quot; &quot; &quot; 4 &quot;</td>
</tr>
</tbody>
</table>

The formula for B is suggested by the analytical figures (A) for the impure compound. Analyses of other compounds suggest that after crystallisation the vanadyl malate complex could be 1:1.

<table>
<thead>
<tr>
<th>Pyrogallol Complexes of Vanadium (IV)</th>
<th>% V</th>
<th>% C</th>
<th>% H</th>
<th>% H₂O</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>20.0</td>
<td>36.3</td>
<td>3.1</td>
<td>7.3</td>
<td>analysis found</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>13.6*</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>20.5</td>
<td>36.2</td>
<td>2.6</td>
<td>12.7</td>
<td>calc. for (VO)₄(C₆H₄O₃)₅ 7H₂O</td>
</tr>
</tbody>
</table>

The compound may lose (one molecule of) pyrogallol on crystallisation as the catechol complex appears to do.
### Table 8. (contd.)

<table>
<thead>
<tr>
<th>Vanadyl Gluconate</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>% V</td>
<td>% C</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>A 20.8</td>
<td>25.0</td>
</tr>
<tr>
<td>B 21.1</td>
<td>24.8</td>
</tr>
<tr>
<td>C 19.8</td>
<td>27.9</td>
</tr>
<tr>
<td></td>
<td>18.6</td>
</tr>
<tr>
<td></td>
<td>17.5</td>
</tr>
</tbody>
</table>

A 1:1 complex may be formed on crystallisation.

<table>
<thead>
<tr>
<th>Vanadyl Salicylic Acid</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>% V</td>
<td>% C</td>
</tr>
<tr>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td>A 20.3</td>
<td>37.9</td>
</tr>
<tr>
<td>B 20.5</td>
<td>37.9</td>
</tr>
<tr>
<td>C 22.9</td>
<td>37.7</td>
</tr>
<tr>
<td></td>
<td>21.2</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The structure of salicylic acid, the results obtained from, and the proposition put forward for, the vanadyl sulphate/(with sodium salicylate) suggest that the acid should form a 1:1 complex when pure.
TABLE  8. (contd.)

<table>
<thead>
<tr>
<th>Vanadyl Mucate</th>
<th>% V</th>
<th>% C</th>
<th>% H</th>
<th>% H₂O</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>15.9</td>
<td>22.0</td>
<td>4.4</td>
<td>16.4</td>
<td>as prepared</td>
</tr>
<tr>
<td>B</td>
<td>15.7</td>
<td>22.1</td>
<td>3.1</td>
<td>16.6</td>
<td>calc. for VO(\text{C}_6\text{H}_4\text{O}_8) \text{3 H}_2\text{O}</td>
</tr>
</tbody>
</table>

The analyses suggest the formation of a 1:1 complex.

<table>
<thead>
<tr>
<th>Vanadyl Mandelate</th>
<th>% V</th>
<th>% C</th>
<th>% H</th>
<th>% H₂O</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>18.8</td>
<td>41.4</td>
<td>3.8</td>
<td>19.8</td>
<td>as prepared</td>
</tr>
<tr>
<td>B</td>
<td>18.6</td>
<td>41.0</td>
<td>4.2</td>
<td>11.0</td>
<td>calc. for (VO)\text{6 (C}_6\text{H}_6\text{O}_3\text{)} \text{7 10 H}_2\text{O}</td>
</tr>
<tr>
<td>C</td>
<td>21.4</td>
<td>40.3</td>
<td>4.6</td>
<td>10.7</td>
<td>&quot; &quot; VO (C₆H₆O₃) 2 H₂O</td>
</tr>
</tbody>
</table>

The structure of mandelic acid, the results obtained from, titration and the proposition put forward for, the vanadyl sulphate/(with sodium mandelate) suggest that the acid should form a 1:1 complex, when the complex is pure.

Footnote: * This signifies the percentage water absorbed by the complex after drying over P₂O₅ at 100°C.
II (g) Molecular Weights.

Molecular weight determinations were carried out using the freezing point depression method. Approximately 0.1 gm of the complex was dissolved in about one ml of de-ionised water for the determination. The apparatus used consisted of an iron-constantan thermocouple (with wet ice as the reference), a Leeds and Northrup potentiometer and Cambridge moving-spot galvanometer and scale. Table 9 lists the empirical formula weights of the complexes as determined from the analyses, and the molecular weights found.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Empirical Formula Weight</th>
<th>Molecular Weight Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>with water</td>
<td>neglecting water</td>
</tr>
<tr>
<td>(VO)$_6$(D-tartrate)$_6$ (dioxane)$_5$ 9H$_2$O</td>
<td>1748</td>
<td>1586</td>
</tr>
<tr>
<td>(VO D-tartrate(dioxane)$_{5/6}$)</td>
<td></td>
<td>290</td>
</tr>
<tr>
<td>VO (meso-tartrate) H$_2$O</td>
<td>233</td>
<td>197</td>
</tr>
<tr>
<td>(VO)$_2$Na$_3$ (D-tartrate)$_2$</td>
<td>665</td>
<td>525</td>
</tr>
<tr>
<td>VO Na$_2$D-tartrate)</td>
<td></td>
<td>263</td>
</tr>
<tr>
<td>(VO)$_3$(Citrate)$_2$ 5H$_2$O</td>
<td>675</td>
<td>585</td>
</tr>
<tr>
<td>(VO) Na$_2$(citrate) 7H$_2$O</td>
<td>428</td>
<td>302</td>
</tr>
</tbody>
</table>
Magnetic moments were calculated using a computer programme (appendix 1) using magnetic measurements made at room temperature. The formulae used to calculate the diamagnetic correction and to calculate the formula weight per vanadyl ion were those obtained from the analyses carried out upon the compounds. Table 10 shows the complexing agent, the molar susceptibility, the calculated magnetic moment and the reference. Values obtained by earlier workers are included where they were available.

**TABLE 10.**

<table>
<thead>
<tr>
<th>Complexing Agent</th>
<th>Corrected Molar Susceptibility $\chi_a$</th>
<th>Room Temp. Magnet Moment $\mu$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-tartaric acid</td>
<td>$1.26 \times 10^{-3}\ast$</td>
<td>$1.725$ B.M.</td>
<td>present work</td>
</tr>
<tr>
<td></td>
<td>$1.218 \times 10^{-3}$</td>
<td>$1.74$ B.M.</td>
<td>ref.7</td>
</tr>
<tr>
<td>meso-tartaric acid</td>
<td>$1.365 \times 10^{-3}$</td>
<td>$1.796$</td>
<td>present work</td>
</tr>
<tr>
<td></td>
<td>$1.28 \times 10^{-3}$</td>
<td>$1.735$</td>
<td>ref.7</td>
</tr>
<tr>
<td>sodium D-tartrate</td>
<td>$1.077 \times 10^{-3}$</td>
<td>$1.595$</td>
<td>present work</td>
</tr>
<tr>
<td></td>
<td>$1.391 \times 10^{-3}$</td>
<td>$1.77$</td>
<td>ref.7</td>
</tr>
<tr>
<td>citric acid</td>
<td>$1.152 \times 10^{-3}$</td>
<td>$1.65$</td>
<td>present work</td>
</tr>
<tr>
<td>tri-sodium citrate</td>
<td>$1.426 \times 10^{-3}$</td>
<td>$1.836$</td>
<td>&quot;</td>
</tr>
<tr>
<td>mandelic acid</td>
<td>$0.977 \times 10^{-3}$</td>
<td>$1.526$</td>
<td>&quot;</td>
</tr>
<tr>
<td>malic acid</td>
<td>$1.0395 \times 10^{-3}$</td>
<td>$1.579$</td>
<td>&quot;</td>
</tr>
<tr>
<td>gluconic acid</td>
<td>$0.918 \times 10^{-3}$</td>
<td>$1.480$</td>
<td>&quot;</td>
</tr>
<tr>
<td>salicylic acid</td>
<td>$0.673 \times 10^{-3}$</td>
<td>$1.266$</td>
<td>&quot;</td>
</tr>
<tr>
<td>pyrogallol</td>
<td>$1.565 \times 10^{-3}$</td>
<td>$1.929$</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

* The complex contains dioxane.
II (i) *pK* Values.

Previous workers (7) had found that when the vanadyl, meso- and D-tartrate complexes were titrated with dilute sodium hydroxide, the titration curves obtained differed for the two complexes. In this present work all the complexes prepared were titrated with approximately 0.1 molar sodium hydroxide and then backtitrated with approximately 0.1 molar hydrochloric acid. The complexes prepared from the salts of acids were titrated with acid then back-titrated with alkali. (For a comparison, the ligands were also titrated). The graphs of the titrations are given in figures: 8, 9, 10, 11 and 12.

From the graphs the *pK* values of the ligands and complexes were determined. These values were obtained using the relationship

\[
pK = pH
\]

at the half neutralisation point.

The problems encountered in these titrations were the same as in the titrations of vanadyl sulphate. (\(pK > 4\))

*pK* is defined as the negative of the logarithm of the acid dissociation constant, \(Ka\). The *pK* of the complexes gives the relative strength of the complexes as acids. The free energy change of the reaction is related to the *pK*.

A low *pK* value indicates that the compound is a strong acid, while a large *pK* value shows that the complex is a weak acid.
TITRATION OF TARTARIC ACID COMPLEXES

Figure 8

MOLES OF TITRANT PER MOLE OF LIGAND or VO^{2+}
Figure 10

pH

Moles of Titrant per Mole of Ligand or VO$^{2+}$
Figure 11

\[ \text{pH} \]

\[ \text{Na}_2 \text{citrate} \]

\[ \text{VO Na}_2 \text{citrate} \]

\[ \text{VO Na}_2 \text{citrate} \]

\[ \text{MOLES OF TITRANT PER MOLE OF LIGAND or VO}^{2+} \]
Figure 8 gives the titration curves of the vanadyl meso- and D-tartrate complexes with sodium hydroxide it also gives the graphs of the titration of meso-tartaric acid with sodium hydroxide and the back titration of the vanadyl meso-tartrate complex with hydrochloric acid. The corresponding graphs for the titrations of D-tartaric acid and vanadyl D-tartrate show the same 'behaviour' pattern and have consequently not been included.

An interesting feature is the fact that graphs for the titrations of the complexes prepared from

D-tartaric acid,
citric acid

and their sodium salts

(Figs. 8, 9, 10, 11) show the same trends for titrations with the same titrant (i.e. HCl & NaOH).
<table>
<thead>
<tr>
<th>Complexing Agent</th>
<th>pK of ligand</th>
<th>pK&lt;sub&gt;1&lt;/sub&gt;</th>
<th>pK&lt;sub&gt;2&lt;/sub&gt;</th>
<th>pK&lt;sub&gt;3&lt;/sub&gt;</th>
<th>No. of equivalence points in back titration</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-tartaric acid</td>
<td>3.68</td>
<td>4.15</td>
<td>6.2</td>
<td>7.5</td>
<td>3</td>
</tr>
<tr>
<td>meso-tartaric acid</td>
<td>3.76</td>
<td>4.10</td>
<td>4.10</td>
<td>8.1</td>
<td>3</td>
</tr>
<tr>
<td>Na D-tartrate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>citric acid</td>
<td>4.63</td>
<td>3.75</td>
<td>4.18</td>
<td>9.58</td>
<td>3</td>
</tr>
<tr>
<td>Tri-sodium citrate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Catechol</td>
<td>* 9.45</td>
<td>5.1</td>
<td></td>
<td></td>
<td>1 only 1 forward step</td>
</tr>
<tr>
<td>mandelic acid</td>
<td></td>
<td>4.75</td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>malic acid</td>
<td>4.20</td>
<td>4.40</td>
<td>6.37</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>pyrogallol</td>
<td></td>
<td>5.40</td>
<td></td>
<td></td>
<td>1/2</td>
</tr>
<tr>
<td>salicylic acid</td>
<td></td>
<td>3.6</td>
<td>5.05</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>gluconic acid</td>
<td></td>
<td>6.2</td>
<td>4.3</td>
<td>5.0</td>
<td>6.3</td>
</tr>
<tr>
<td>mucic acid</td>
<td>4.15</td>
<td></td>
<td>6.82</td>
<td>6.87</td>
<td>2</td>
</tr>
<tr>
<td>lactic acid</td>
<td>3.72</td>
<td>4.2</td>
<td>5.18</td>
<td>5.84</td>
<td>3</td>
</tr>
</tbody>
</table>

* second pK value
II (j) Infra-red Spectra.

Infra-red spectra were run on all the complexes and ligands involved.

The stretching frequencies of metal-oxygen double bonds may generally be found between 900 and 1100 cm$^{-1}$(4). The strong bond at 955 cm$^{-1}$(37) in vanadyl hydroxide was attributed to the V=O stretching vibration.

Owing to the complexity of the ligands and the strong effect that adjacent graphs have upon the stretching frequency of a particular group, the interpretation of the spectra is rather involved.

The spectra of vanadyl hydroxide and vanadyl sulphate were recorded to enable a comparison to be made with the spectra of the complexes.
V-O STRETCHING FREQUENCY.

Table 12 lists, for the various complexing agents used, the bands assigned to the V-O stretching frequency, and the width and intensity of the band.

<table>
<thead>
<tr>
<th>Complexing Agent</th>
<th>Remarks</th>
<th>Frequency of Absorption (cm(^{-1}))</th>
<th>Intensity of Band</th>
<th>Width of Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>sodium D-tartrate</td>
<td>impure and recrystallised</td>
<td>930</td>
<td>v strong</td>
<td>sharp</td>
</tr>
<tr>
<td>tri-sodium citrate</td>
<td>recrystallised from water and ethonal with NaOH added</td>
<td>940</td>
<td>strong</td>
<td></td>
</tr>
<tr>
<td>tri-sodium citrate</td>
<td>recrystallised from water and ethonal</td>
<td>945</td>
<td>v strong</td>
<td></td>
</tr>
<tr>
<td>vanadyl hydroxide</td>
<td></td>
<td>960</td>
<td>strong</td>
<td></td>
</tr>
<tr>
<td>citric acid</td>
<td></td>
<td>960</td>
<td>v strong</td>
<td>medium</td>
</tr>
<tr>
<td>D-tartaric acid</td>
<td>recrystallised, dissolved in water and solvent evaporated</td>
<td>960</td>
<td></td>
<td></td>
</tr>
<tr>
<td>malic acid</td>
<td></td>
<td>965</td>
<td>strong</td>
<td>medium</td>
</tr>
<tr>
<td>salicylic acid</td>
<td></td>
<td>965</td>
<td></td>
<td></td>
</tr>
<tr>
<td>mesotartaric acid</td>
<td></td>
<td>965</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D-tartaric acid</td>
<td>recrystallised</td>
<td>970</td>
<td></td>
<td>sharp</td>
</tr>
<tr>
<td>lactic acid</td>
<td></td>
<td>970</td>
<td></td>
<td>medium</td>
</tr>
<tr>
<td>pyrogallol</td>
<td></td>
<td>970</td>
<td>medium</td>
<td></td>
</tr>
<tr>
<td>mucic acid</td>
<td></td>
<td>972</td>
<td>v strong</td>
<td></td>
</tr>
<tr>
<td>sulphate (vanadyl sulphate)</td>
<td></td>
<td>980</td>
<td>strong</td>
<td>sharp</td>
</tr>
<tr>
<td>tri-sodium citrate</td>
<td>recrystallised, dissolved in water &amp; evaporated</td>
<td>980</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Complexing Agent</td>
<td>Remarks</td>
<td>Frequency of absorption of Band</td>
<td>Intensity of Band</td>
<td>Width of Peak</td>
</tr>
<tr>
<td>------------------</td>
<td>---------</td>
<td>---------------------------------</td>
<td>------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>gluconic acid</td>
<td></td>
<td>995 cm(^{-1})</td>
<td>weak</td>
<td>medium to broad</td>
</tr>
<tr>
<td>catechol</td>
<td>1,000 &quot;</td>
<td>weak</td>
<td>1,080 &quot;</td>
<td>weak</td>
</tr>
</tbody>
</table>
Infra-red Spectra - General.

Based upon the spectra determined for the complexing agents and the complexes, the following interpretations for the properties of groups of compounds can be made:

Polymeric association of intermolecular OH hydrogen—bonds occurs in the spectra of both the ligand and the complex for most of the complexing agents.

The strong band due to aliphatic acids C=O stretching (1725 - 1700 cm\(^{-1}\)) present in the spectra of all the acids, except salicylic, is changed to the antisymmetric COO\(^{-}\) band in the complex. Salicylic acid displays a strong band at 1640 cm\(^{-1}\) due to acidic intermolecular hydrogen bonds. However, the symmetric COO\(^{-}\) band is not present in the spectra of all the complexes. Complexes prepared from acids displaying this band are the vanadyl complexes with mandelic, salicylic, lactic, gluconic and the tartaric acids.

All the salts and their complexes display the symmetric and anti-symmetric COO\(^{-}\) stretching frequency bands.
Infra-red Spectra.

Co-ordinating Groups and Complexes.

D-Tartaric Acid.

There is no unexpected spectral change in going from the acid to complex or between the complexes with or without dioxane.

The only points of interest are ——

(i) the small shift (20 cm\(^{-1}\)) from the acid to the complexes of the CO stretching band near 1100 cm\(^{-1}\).

(ii) There is a small shift of several of the bands between the complex with dioxane and that without dioxane.

Sodium D-Tartrate.

There is very little change between the spectra of the two crystallised complexes, \((\text{VO})_2 \text{Na}_3 (D\text{-tartrate})_2\) and \(\text{VONa}_2 D\text{-tartrate}\), or even between these and the spectra of the uncrystallised complex. However, there is generally a significant change in the frequency in going from the ligand to the corresponding band in the complexes.

meso-Tartaric Acid.

The main feature of these spectra is the absence of the bands due to hydroxyl groups in the complex which are present in the spectrum of the ligand.

The above results, together with:

(i) the molecular weight determination,

(ii) a study of the stereochemistry of the ligand and the explanation put forward for the titrations of vanadyl sulphate, (see "Discussion") and

(iii) the empirical formula obtained from the analysis;
suggest that there is extensive intermolecular association, with the OH group filling some coordination positions of a vanadyl ion.

**Citric Acid.**

As with the meso-tartaric acid the spectrum of this acid contains bands apparently due to the OH group. These bands are absent in the complex. This suggests that the citric acid's hydroxyl group acts as a chelating agent in the complex.

**Tri-sodium Citrate.**

There are small shifts in all the important frequencies in going from the ligand to the complex. However, the spectra of the complexes crystallised with and without the addition of sodium hydroxide differ significantly. This is especially so for the symmetric and anti-symmetric COO\(^-\) bands. There is a difference in the V=O stretching frequency in the two complexes.

**Catechol.**

The ligand displays a band due to single bridge intermolecular H-bonds, whereas the complex does not.

Most of the bands in the spectrum of catechol which may be assigned (even those due to the benzene ring, etc.) are absent from the spectrum of the complex.

**Pyrogallol.**

On the other hand, most of the peaks of pyrogallol are also observed in the spectrum of the complex. The exceptions are the band due to intramolecular hydrogen bonds. Since the complex appears to be 1:1 from the analysis, this peak would not be
expected in the spectrum of the complex. The phenolic band near 1200 cm\(^{-1}\) is also absent from the spectrum of the complex.

**Mandelic Acid.**

There is a change in the nature of the OH group hydrogen-bonding from single bonds in the acid to polymeric association in the complex. The OH stretching frequency (1070) present in the spectrum of the acid does not appear in the spectrum of the complex. This suggests that the hydroxyl group ionises on formation of the complex, forming the alkoxide. Mandelic acid would thus act as a di-basic acid. This is in agreement with the results for the vanadyl sulphate titrations.

**Salicylic Acid.**

The spectrum of the acid contains bands due to the CO stretching of phenol, and chelate compound's strong intramolecular bonds. The phenolic band near 1200 cm\(^{-1}\) also appears to be present in the spectrum of the complex. This would not normally be expected if a 1:1 complex was formed as the analysis suggests. This band may be explained by the apparent presence of excess ligand in the complex (VO : salicylate = 8:9). (\(^{33}\))

**Gluconic Acid.**

The acid shows bands due to intramolecular hydrogen-bonds, free alcoholic OH, chelate compound strong intramolecular bonds and secondary alcohol OH deformation. None of these bands is present in the spectrum of the complex. Alcoholic CO stretching bands are present in the spectra of the acid and the complex.

**Mucic Acid.**

The spectra of the acid and the complex contain bands attributable to \(^{2}\)OH CO stretching and OH deformation vibrations.
Melting Points.

The tartrate and citrate complexes were heated to 300°C under controlled conditions. None melted, but the mauve powder of the vanadyl sodium D-tartrate complex turned pale mauve, then brown, suggesting decomposition without melting.

Continuous Variation Spectroscopy.

An attempt to investigate the possible nature of the complexes using the continuous variation spectra method was unsuccessful. No suitable peaks were found in either the visible or ultra-violet regions of the spectrum.
III - DISCUSSION
III - DISCUSSION.

III (a) pH Titrations of Vanadyl Sulphate.

Since a pH fall only occurred in the titration with some 'bases', then the pH fall may be attributed to a change occurring within the ligand rather than within the vanadyl complex (as it exists in the solution).

As expected none of the aliphatic polyhydroxy-alcohols and sodium carboxylates used gave a pH fall. The carboxylates may have formed complexes with the vanadyl ion, but this would not be expected to result in a drop in pH, as the structure suggests there is no change possible in the nature of the titrant. As aliphatic alcohols are weaker acids than water, then ionisation of the alcohols to form complexes is unlikely. There is little likelihood of any of the alcohols displacing the co-ordinated water from the vanadyl ion, as water is such a strong co-ordinating group.

A pH fall was not given in the titration of vanadyl sulphate with the four sodium hydroxy carboxylates—sodium lactate, glycollate, p-hydroxy benzoate and coumarate.

The structures of the two aromatic acids would prevent the corresponding carboxylates from behaving as bidentate ligands. Co-ordination of the anions to vanadyl ions through the carboxylate groups probably did occur, and co-ordination through the phenolic groups may also have occurred. However, the absence of a pH fall suggests that the phenolic groups did not ionise.

On the other hand the aliphatic salts of lactic acid (CH₃CH(OH)COOH) and glycolic acid (CH₂(OH)COOH) could only act as bidentate ligands in...
co-ordination compounds by the formation of a five-membered ring which would be unstable. (Figure: 13) This explains the failure of the hydroxyl group, a weak acid, to ionise. (The above acids would then behave only as monobasic acids.)

![unstable 5-membered ring](image)

Figure: 13

The other hydroxy carboxylates used gave pH minima in the titrations. The aliphatic compounds all have B-hydroxyl groups to carboxyl groups; this would permit the formation of a stable six-membered ring through the carboxylate and hydroxyl groups. The experimental results suggest that the hydroxyl group ionises, forming an alkoxide ion, with the release of a proton; this would cause a fall in the pH. This proposition could explain the experimental results obtained in the citrate, tartrate, malate, malonate and mucate titrations. In three of the above anions, namely citrate, tartrate, and malate - the presence of an \( \alpha \)-carboxyl group would increase the acid strength of the hydroxyl group.

An explanation for the variation in the titrations using the above proposition is as follows: The citrate has four functional groups;
complexing (with a vanadyl ion) could occur through a terminal carboxyl group and the central carboxyl group. The other terminal carboxyl group and the ionised hydroxyl group could form a complex with another vanadyl ion.

The maximum fall in pH would occur when the ratio of citrate to vanadyl ions is 1:2. The addition of more titrant would result in a fall in the free hydrogen ion concentration due to dilution, and the effect of the dissociation constant of citric acid upon the free citrate's absorbing (free)hydrogen ions.

Similarly the meso-tartaric and mucic acids behave as tetra-basic acids, complexing with two vanadyl ions. However, here the complexing to vanadyl ions occurs through each carboxyl group and the B-hydroxyl group as an alkoxide ion. Again the maximum free hydrogen ion concentration would occur when the titrant: vanadyl-ion ratio is 1:2. Fig. 14.

Unlike the above polycarboxylic acids, the monocarboxylic acid used (i.e. gluconic acid) may only form one complex through a carboxyl group and its B-alkoxide ion. The maximum hydrogen ion concentration would thus occur when the vanadyl : gluconate ratio is 1:1.

Stereochemical factors appear to be the reason for the difference in the volume of titrant required to attain the pH minima for the vanadyl sulphate titrations with sodium meso- and D-tartrates. The result of the titrations suggest that while the sodium meso-tartrate acts as a di-basic acid, forming a 2:1 vanadyl : tartrate complex, the sodium D-tartrate behaves as a monobasic acid, with only one hydroxyl group undergoing ionisation. The difference in the behaviour of the isomers does not appear attributable to the different configurations of the meso- and
Figure 14

Suggested structures for the proposed complexes formed in the vanadyl titrations.
Both structures have the same steric factors relative to complex formation. Also the difference in the behaviour pattern of the stereoisomers does not appear to be based upon the stabilities of the different conformations of the six-membered rings formed. These rings have an axis of symmetry. Models suggest that stress free conformations are available for complexes prepared from both stereoisomers. The only apparent difference between the isomers is due to the meso-tartrate's formation of complexes which may have conformations with both rings in the low-energy chair or boat conformations. However, the D-tartrate can form stable bi-cyclic complexes with only one ring in the chair or boat form; one ring is always distorted and may never have the symmetry of a chair or boat conformation. The D-tartrate's apparent inability to form two rings in low-energy conformations appears to be the reason for the difference in the behaviour of the meso- and
D-tartrates.

The small volume of titrant required to attain the minimum pH in the titration with sodium malate cannot readily be explained by the above proposition or by any other argument. Complex formation between the ionised hydroxyl group and the B-carboxylate is possible and could be the reason for the pH fall. The remaining carboxylate group could co-ordinate to another vanadyl ion. Co-ordination of the two carboxyl groups to the one vanadyl ion is also possible giving a seven-membered ring. This structure would not allow a pH fall to occur consistent with the above theory.

The aromatic hydroxy carboxylates which gave a pH fall were the sodium salicylate, benzilate and mandelate. The volume of titrant required to give the maximum pH fall was approximately the same for each salt.

The salicylate could form a stable six-membered ring, whereas the mandelate and benzilate could form less stable five-membered rings. (Fig. 16) The reason for the possible stability of the latter complexes, as suggested by experimental results, is resonance stabilisation. The benzene ring, or rings, adjacent to the five-membered ring of the complex would permit electrons to be donated to, or withdrawn from, the complex ring so as to increase the stability of the complex. Experimental results suggest no hydroxy aliphatic acids formed complexes with five-membered rings. (Proposed Structures Figures 16a and 16b.)

Pyrogallol and catechol caused pH falls in the titration of vanadyl sulphate, whereas resorcinol and phenol did not. The phenols, pyrogallol and catechol, have ortho-phenolic groups, but the other do not.

The phenols in order of decreasing acid strength are resorcinol,
R = H  mandelate
R = C₆H₅  benzilate

Salicylate
phenol and catechol. The likely reason for the pH fall during the titrations is possible complex formation with co-ordination occurring through the ortho-phenolic groups. It has been suggested (12) that $[\text{VOA}]$ and $[\text{VOA}_2]^{2-}$ type complexes are formed when solutions of vanadyl sulphate and catechol ($H_2A$) are titrated with potassium hydroxide. The acid strength of the catechol (in this project) was limited by the absence of a strong base. This would appear to limit complex formation. A large titration was required to attain the pH minimum. The vast excess of catechol over that required for a 1:1 ratio of VO : catechol may have slowly (through its effect upon the equilibrium constant) forced complex formation. However, complex formation may have been slow due to the weak acid strength of the phenolic groups. According to this reasoning a similar argument could be made for the titration of vanadyl sulphate with pyrogallol.

Other workers (7) investigating titrations of vanadyl sulphate with pyrogallol and catechol obtained results which differ from those obtained in the present work. They gave no explanation for their large titrations nor is the author able to offer an explanation for their results.
Summary of Discussion of Vanadyl Sulphate Titrations

In the titrations of vanadyl sulphate, proton release by the liberation of a hydrogen from hydroxyl groups in the salts appear to be the reason for the pH falls recorded. Ionisation occurs only if a stable ring can be formed through the vanadium. In the case of the salts - sodium citrate, meso-tartrate, and mucate - the low titration has been explained in terms of the apparent formation of a two-to-one VO : titrant complex. The gluconate's large titration depends upon the formation of a 1:1 complex, while steric factors within the complex appear to govern the titration with the D-tartrate.

The salicylate appears to form a stable complex with a six-membered ring.

The stability of the complexes formed with five-membered rings from titrations with benzilate and mandelate are explained in terms of resonance stabilisation due to the benzene ring(s) on the α-carbon to the carboxylate group.

In each case the remaining co-ordination positions of the vanadyl ion are probably filled by water, and co-ordination of sulphate is unlikely.

The limited experiments carried out suggest the following conclusion: There is a pH fall only when vanadyl sulphate is titrated with -

(a) aliphatic hydroxy carboxylates with a β-hydroxyl group;

or

(b) aromatic hydroxy carboxylates which have either:

(i) a hydroxyl group ortho- to a carboxyl group; or

(ii) an OH and benzene ring which are α- to the carboxyl group;

or

(c) phenols with ortho-dihydroxy groups.
(b) pH Fall in Titrations of Vanadyl Sulphate.

The maximum fall in the pH is not explained by the assumption made in the previous section concerning the volume of titrant required to attain the pH minimum. (The pH fall displays no pattern which would suggest a possible explanation of the results.) The absence of a pattern is not 'unreasonable' as the pH fall would depend upon a large number of factors. These include the number of protons released by the titrant anions, the pH of the titrant, the activity of the hydrogen ion, and the dissociation constants of the titrant and complex.
III (c) Structure of The Complexes.

Vanadyl D-tartrate.

Crystallised vanadyl D-tartrate complex forms a one-to-one vanadium : D-tartrate complex. Crystallisation was carried out several times from aqueous solution by the addition of the non-solvent dioxane. The analysis of the compound suggested the empirical formula $(\text{VO})_6(\text{D-tartrate})_6(\text{dioxane})_5\cdot 9\text{H}_2\text{O}$. Two separate recrystallisations of this complex gave complexes with different analyses. This suggests that the nature of the complex is dependent upon the conditions for crystallisation. (One of the recrystallised compounds had the empirical formula $\text{VO}(\text{D-tartrate})(\text{dioxane})_2\cdot \text{H}_2\text{O}$.)

Structure: Vanadyl D-tartrate.

As the crystallised complex has a VO : D-tartrate ratio of 1 : 1 and the carboxylic acid groups of the tartrate are the strongest acidic functional groups, then the complex would have the two carboxyl groups co-ordinated to the vanadyl ion. This would give electroneutrality.

The stereochemistry of the D-tartaric acid and the vanadyl ions, in which the $\text{O} \rightarrow \text{V} - X$ angle (45) is greater than $90^\circ$ (X being an equatorial ligand), could permit one of the hydroxyl groups to act as a co-ordinating group. This would occur by means of one of the hydroxyl oxygen lone electron-pairs co-ordinating to the vanadium. Here the D-tartaric acid would behave as a tridentate ligand towards the vanadyl ion; the co-ordination in the above compound occurs in the equatorial positions of the vanadyl ion; the carboxyl groups trans-co-ordinate in positions of the vanadyl ion. Figure: 17.
A model of this molecule was prepared (43) and found to have a high stress. This stress was mainly due to the formation of a five-membered ring by the hydroxyl group. The complex without this hydroxyl group co-ordinated to the vanadium had less stress. The amount of stress depends upon the vanadium to ligand bond-length and the O-V-O bond angle.

The complex formed by the co-ordination of the carboxyl oxygens into cis equatorial positions of the vanadium gives a stable seven-membered ring. One of the possible conformations of this molecule is seen in Figure: 18. The hydroxyl groups could co-ordinate to another vanadyl ion through an oxygen lone-pair of electrons. Several different conformations of this complex are possible.
Figure 18.
The more sterically favoured of the proposed configurations for the vanadyl D-tartrate complex.
A different conformation of this configuration could have a hydroxyl hydrogen near the vanadium. Figure 19

![Figure 19](image)

This complex with the carboxyl groups co-ordinated into cis-equatorial vanadyl co-ordination positions (as in Fig. 19) appears to be free of any significant stress.

A configuration with a carboxyl group co-ordinated to the vacant axial position of the vanadyl ion is unlikely, as the axial position co-ordinates only weakly.
Vanadyl meso-Tartrate.

The analysis carried out upon this compound suggests the formation of a one-to-one VO : meso-tartrate complex. This is in agreement with earlier work (7).

The two carboxyl groups of the meso-tartrate could co-ordinate to the one vanadyl ion in the stable equatorial positions and appear to co-ordinate in cis- positions on the vanadyl ion. This would permit the two hydroxyl groups to possibly co-ordinate cis- to another vanadyl ion and would enable the formation of a polymeric molecule. This could help to explain the high experimental molecular weight. The proposed structure is shown in the Figure 20. The conformation of the proposed structure would have equivalent hydroxyl hydrogens and would be in agreement with the results of the sodium hydroxide titration of the complex.
Figure 20.
The configuration of vanadyl *meso*-tartrate proposed on the basis of the analysis.

N.B. The red prolongation emanating from the vanadium below the plane of the ring (i.e. pointing downwards) is attached only to support the framework for photography purposes.

Legend: V green
C black
O red
H white
Vanadyl Sodium D-tartrate.

The complex appears to have the empirical formula: 
\[(\text{VO})\text{Na}_2(\text{D-tartrate}) \ 3 \ H_2O\] when crystallised from water or from water and \text{n-propanol}. There appears to be a slow loss of sodium ions from the complex, even when it is crystallised from solutions to which a little dilute sodium hydroxide has been added.

Structure: \text{VONa}_2 \text{ D-tartrate}.

The analysis of the complex gives the empirical formula as \text{VONa}_2(\text{D-tartrate}); consecutive crystallisations of the complex result in the slow loss of sodium ions. This suggests that the two sodium ions are fairly strongly held in the complex, and further infers that they are attached to the tartrate, rather than being present in some other form as (say) sodium hydroxide.

The apparent ionisation of a sodium D-tartrate hydroxyl group during the titration of vanadyl sulphate solution, and the above evidence, suggest that all four functional groups of the tartrate are ionised in the complex. Further support for this theory comes from the loss of one mole of sodium ions from the vanadyl sodium citrate complex (see Page 62). It appears that the complex is of the form:

\[
\begin{array}{c}
\text{H} \\
\text{O} \quad \text{C} \quad \text{COO} \\
\text{OOC} \quad \text{C} \quad \text{O} \\
\text{H}
\end{array}
\]

\[
\text{VO}^{2+} \quad \text{Na}_2^{+}
\]
Recrystallisation from solution (free from added sodium hydroxide) appears to result in the slow loss of sodium ions and formation of hydroxyl groups. If the theory is correct, then the vanadyl ions are probably co-ordinated to the two carboxyl groups or to a carboxyl and B-hydroxyl group. The formation of a complex through the two hydroxyl groups, or a carboxyl and an α-hydroxyl group, is unlikely as this would result in the formation of an unstable five-membered ring. Water could occupy unfilled co-ordination positions of the vanadyl ion.

Vanadyl Citrate.

A three-to-two VO : citrate ratio is given by the empirical formula

\[(\text{VO})_3 (\text{Citrate})_2 \quad 5\text{H}_2\text{O}\]

suggested by the analysis. The bi-valent vanadyl ion and tri-basic acid would then give a complex with electroneutrality.
Vanadyl Sodium Citrate.

This was prepared as a black powder but, after separation of impurities, a blue solid with a VO : Na ratio of 1:3 remained. When crystallised from aqueous solution by the addition of the non-solvent ethanol, the compound was found to have the empirical formula:

\[ \text{VONa}_2 \text{Citrate } 3\text{H}_2\text{O}. \]

Structure of Vanadyl Sodium Citrate.

The loss of one mole of sodium ions during the crystallisation procedure, the titration of vanadyl sulphate and the analysis indicate that citric acid probably behaves as tetra-basic acid in the complex. The three carboxyl groups and the hydroxyl group would ionise. There is no evidence to suggest the nature of the complex. However, it appears that complex formation with the vanadyl ion probably occurs through the hydroxyl group. There are two reasons offered for this suggestion. Firstly, it would permit the formation of a stable six-membered ring through one of the terminal carboxyl groups and the alkoxide ion. And secondly, if the aforementioned complex did not form then the alternative, which would be sodium alkoxide, would be unstable.

The rapid loss of the third sodium ion of the complexing agent supports the theory that the only anion in the complex is the citrate. Again, water could fill the remaining co-ordination positions of the vanadyl ion.
Catechol Complexes of the Vanadyl Ion.

The analysis of the complex dried over calcium chloride suggests the empirical formula VO(Catechol)\(_3\) \(3.5\text{H}_2\text{O}\) and the complex, dried at 100°C. and under reduced pressure, has the empirical formula VO(Catechol)\(_2\) \(n\text{H}_2\text{O}\) \(n = 1.5-3\).

Structure Catechol Complexes.

The loss of the mole of catechol on drying gave the VO : Catechol = 1:2 which suggests that the catechol complex has catechol acting as either a mono- or di-basic acid. This would give the complex as (VO catechol) with a second mole of catechol strongly co-ordinated into the molecule. Alternatively, there is the possibility of catechol molecules acting as mono-basic acids co-ordinated to the vanadium. Equilibrium constants for the formation of (VO catechol) and VO(catechol)\(_2\) \(^{2-}\) have been determined in alkline conditions. In both cases the catechol appeared to act as a di-basic acid. The structures:

![Structures](image)

were proposed and would favour the former proposition.

General Complexing Agents.

Analyses of the impure complexes prepared using malic acid, pyrogallol, gluconic acid, salicylic acid, mandelic acid and mucic acid as the complexing agent suggest that the formation of complexes with a VO : ligand ratio of 1:1.
III (d) Molecular Weight.

With the exception of the result for vanadyl meso-tartrate, the results obtained from the molecular weight determinations show that, in solution, the complexes dissociate. The molecular weight in each case is less than the empirical formula weight calculated for the monomer from the analysis. However, from these results, neither the size of the complex, nor the nature of the dissociation of the complexes in water can be determined.

The molecular weight found for the vanadyl meso-tartrate suggests that either the complex is polymeric or that there is a high degree of association in solution. No conclusion as to the size of the complex in the solid state can be drawn from the results. Since all the other (ionic) complexes appear to dissociate in solution, this complex may also dissociate.

A molecular weight determination on vanadyl meso- and D-tartrate complexes carried out by Gellert and Hall (7) gave similar results to those obtained in this work.
III (e) **Titrations of Tartrate Complexes.**

The difference in the titration curves for the vanadyl meso- and D-tartrate complexes titrated with alkali may be explained in terms of the structures proposed for the complexes. It is suggested that the meso-tartrate would have the hydroxyl groups co-ordinated to the same vanadyl ion and the two carboxyl groups co-ordinated to another vanadyl ion. The two hydroxyl groups would be then equivalent (i.e. have identical environment) and so would have the same acid strength. This would cause the 2 hydroxyl groups to ionise at the same pH. Figure 20.

The titration of the D-tartrate complex suggests that the two hydroxyl groups are not equivalent and that the hydrogens have different acid strengths. Such differences are readily explained in the apparently unstable configuration in which the acid behaves as a tridentate ligand.

However, the behaviour of the hydroxyl hydrogens is not as readily explained in the case of the more (sterically) favoured configuration for the complex (with the carboxyl groups co-ordinated _cis_). There are two possible explanations —

either (a) one of the hydroxyl groups may hydrogen-bond to the carbonyl group of one of the carboxyl groups. This would be obtained by rotation of one of the hydroxyl C=O bonds in the conformation shown in Figure 18;

or (b) the complex with this configuration may take up the other conformation suggested for this complex. Figure 19. The hydroxyl hydrogen near the _vanadium_ would be less readily titrated because of the steric hindrance of the vanadyl ion and its ligands.

These two explanations for the difference in behaviour of the
vanadyl D-tartrate hydroxyl groups support this configuration.

The conformation associated with explanation (a) has the advantages:

(i) one of the hydroxyl groups is capable of undergoing hydrogen-bonding to a lone electron-pair of either of the carboxyl groups. This could produce the apparent non-equivalence of the hydroxyl groups characteristic of this complex.

(ii) The seven-membered ring of the complex has a plane of symmetry (but the molecule has not, due to the trans positions of the hydroxyl groups). The ring in the conformation suggested in explanation (b) does not have a plane of symmetry.

III (f) Magnetic Moments.

The room temperature magnetic moments for the tartaric acid and sodium citrate complexes are normal for a paramagnetic ion with one 3d electron.

The low magnetic moments for the other complexes may be attributed to the presence of diamagnetic impurities as the complexes had not been purified. These impurities could include vanadium (V) compounds as the complexes were merely separated by the evaporation of the solvent, while the system was open to the atmosphere. However, the low magnetic moment, especially for the sodium D-tartrate complex, may indicate antiferomagnetic interactions in the complexes. It is intended to test these interactions by carrying out a temperature variation magnetic moment.

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APPENDIX

Computer Programme 1.

```
C C R C SKEVINGTON CHEMISTRY 4
C CALCN OF MOLAR SUSEPT. AND MAGNETIC MOMENTS
91 READ,A,B,E
12 READ  2CC
   PRINT  2CC
2CC FORMAT(56H
  2 READ,W,F,DEL
  3 CHI=(A+B*F)/W *1.0E-6
     PRINT4,CHI
  4 FORMAT(29HSUSEPTIBILITY OF SUBSTANCE = E14.6)
  9 READ,WM,AT
  6 CHIM=CHI*WM-DEL
  7 PRINT8,CHIM
  8 FORMAT(15HMOLAR SUSEPT = E14.6)
     CHIAT=CHIM*AT
     U=2.84*SQRTF(CHIAT)
     PRINT10,U
10 FORMAT(18HMAGNETIC MOMENT = E14.6 )
11 GOTO12
END12
```
The acid base titrations of the complexes were carried out upon known weights of the ligand or complex, using standardised NaOH or HCl. (P. 37)

To permit a visual comparison of the titration curves for the various compounds, the scale along the horizontal axis was changed. This was done with the aid of a computer programme. The programme was used to convert the scale from mls. of titrant to:

(i) moles of titrant added per mole of complexing agent,

or (ii) moles of titrant added per mole of vanadyl ions.

The empirical formulae calculated from the analyses of the complexes were used (in their turn) to calculate the equivalent weight of the complexes.

Figures 8, 9, 10, 11, 12 show graphs with the scale along the horizontal axis converted by the above method.

```plaintext
C C R SKEVINGTON CALC OF TITRANT CONCS.
3 READ, CHCI, CNAOH
1 READ 2CC
PUNCH 2CC
2CC FORMAT (5CH
9 VTA = C.2
READ A
2 READ, PH, WT, VW, VA, WM
PUNCH A, WM
1F (PH) 1C, 1C, 11
1C CONC = CHCL
GO TO 41
11 CONC = CNAOH
41 PUNCH 42
42 FORMAT (5H
4 V = VW + VA
ANOM = WT / WM
5 VOLA = VTA * CONC * C.CC1 / ANOM
EPE = VOLA / A
PUNCH A, VTA, VOLA, EPE
8 PI = VW - V
1F (PI) 7, 7, 1
7 VTA = VTA + C.2
VW = VW + C.2
GO TO 5
END
```
FINDING EQUIVALENCE POINTS OF PH TITRATIONS OF OXOVANADIUM (IV) COMPLEXES

DIMENSION V1(9), PH(9)
DIMENSION X1(9), X2(9), Y(9)

READ 91
PUNCH 91
FORMAT (5CH
READ ,N
NO= N-1
PUNCH 8C, N
FORMAT (4HN = ,12)
PUNCH 32
FORMAT (5CH
DO 61 I = 1, N
READ 31, V1(I), PH(I)
CONTINUE
DO 12 I = 1, N
X1(I) = V1(I)
Y(I) = PH(I)
X2(I) = V1(I) * V1(I)
SUPPLIES THE LEAST SQUARES REGRESSION CONSTANTS TO THE
PN=N
SX1=C
SY=C
S12=C
SX2=C
SX1Y=C
SX2Y=C
SX1SQ=C
SX2SQ=C
SYSQ=C.
DO 99 I = 1, N
SX1 = SX1 + X1(I)
SX2 = SX2 + X2(I)
SY = SY + Y(I)
S12 = S12 + X1(I) * X2(I)
SX1Y = SX1Y + X1(I) * Y(I)
SX2Y = SX2Y + X2(I) * Y(I)
SX1SQ = SX1SQ + X1(I) * X1(I)
SX2SQ = SX2SQ + X2(I) * X2(I)
SYSQ = SYSQ + Y(I) * Y(I)
PA = SX1SQ - (SX1 * SX1) / PN
QA = SX2SQ - (SX2 * SX2) / PN
RA = SX1Y - (SX1 * SY) / PN
\[ \begin{align*}
SA &= Sx_2 y - (Sx_2 \cdot Sy) / PN \\
TA &= S12 - (Sx_1 \cdot Sx_2) / PN \\
DEN &= PA \cdot QA - TA \cdot TA \\
A &= (QA \cdot RA - TA \cdot SA) / DEN \\
B &= (PA \cdot SA - TA \cdot RA) / DEN
\end{align*} \]
Computer Programme 3 Notes.

The determination of pK values from acid—base titrations of compounds requires the finding of the equivalence point. To do this a method (46) (not previously used in chemistry) of analysing experimental data was tested with the aid of a computer programme. The programme was used to calculate the co—efficients of the quadratic function, \( y = ax^2 + bx + c \), which would provide the second—degree curve of best fit for a moving arc of the experimental data. The slope at the mid—point of each arc was calculated from the differential equation, \( \frac{dy}{dx} = 2ax + b \). The maximum value of the differential gives the equivalence point. This method pinpointed mathematically the equivalence point which had been approximately located by visual (i.e. graphical) methods.

The results obtained by the two methods did not always correspond. In those cases where the results did not correspond, a repetition of the calculation, using output from the above calculation (namely \( \bar{x}, \frac{dy}{dx} \)) as input, gave results which did correspond. (Here the equivalence point occurs when the 'differential' is zero.)

Further work should remove the small deficiencies in this method.

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