The sign for \( r_4 \) is chosen positive or negative depending on the angle \( \mu_4 \) being acute or obtuse, respectively.

**FIG 2**

**FIG 2.** Equi-\( r_4 \)-contours (see text for definition) in the (\( \phi, \psi \)) plane.

Physically it may be seen that the above method of assigning the sign is equivalent to projecting the point \( C^\alpha_{i-1} \) and \( C^\alpha_{i+1} \) on to the line of intersection of the two planes as given by the vector \( r_4 \), and comparing the projected vector of \( C^\alpha_{i-1} - C^\alpha_{i+1} \) with \( r_4 \). While it might be possible to adopt for the above comparison any vector other than \( C^\alpha_{i-1} - C^\alpha_{i+1} \), we have chosen this here, since, as far as backbone atoms are concerned, \( C^\alpha \) atoms act as convenient reference points and also the progress of the chain is readily reckoned by tracing their path.

Figure 2 gives the equi-\( r \) contours in the (\( \phi, \psi \)) plane. The 'centrosymmetrical' pattern of the contours is also readily understood. For example, the conformation \( \phi = -120^\circ, \psi = -60^\circ \) and \( \phi = +120^\circ, \psi = +60^\circ \) have \( r \) values of \(-60^\circ\) and \(+60^\circ\) respectively.

A more detailed application of these ideas along the lines of our earlier analysis, including statistical distribution of the angle \( v \), is in progress and will be reported in due course.


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**FIVE COORDINATE OXOVANADIUM(IV) COMPLEXES**

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**INTRODUCTION**

It is well known that the hydrazide residue in the hydrazones can react with metal ion either in keto or in the enol form. Hydrazones derived from isonicotinoyl hydrazide have been used as chelating agents. Complexes of oxovanadium (IV) and oxovanadium (V) with benzenimidazoles and Schiff bases have been studied. It is apparent from the literature that there are quite a few scattered examples of vanadium complexes with hydrazones. It is therefore appropriate to study complex formation of oxovanadium (IV) with the following hydrazones.

**EXPERIMENTAL**

Vanadyl sulphate, isonicotinic acid hydrazide were of reagent grade. The substituted salicylalde-
hydres and acetophenones were prepared by standard methods. Hydrazones were prepared by mixing equimolar mixture of hydrazide and aldehyde or ketone in the absolute ethanol. The solid products obtained were recrystallised from ethanol.

The complexes were prepared by mixing the alcoholic solution of vanadyl sulphate (0.1 mole) with alcoholic solution of ligand (0.2 mole). The mixture was heated on a water bath for an hour. The precipitated complex was filtered and washed successively with small portions of warm aqueous alcohol to remove the excess of the ligand. The complexes are then dried in a desiccator over phosphorus pentoxide.

Vanadium in the complexes was estimated as V₂O₅, by precipitating vanadium hydroxide and igniting it to pentoxide. Nitrogen was estimated by the microanalytical method.

The elemental analysis is shown in Table I.

**Table I**

<table>
<thead>
<tr>
<th>Ligand No.</th>
<th>Complex No.</th>
<th>Empirical formula</th>
<th>Metal %</th>
<th>Nitrogen %</th>
<th>Magnetic moment at 298°K μeff B.M.</th>
<th>Important IR frequencies (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>VIII</td>
<td>VO(C₄H₆N₅O₃)₃</td>
<td>9·61</td>
<td>15·86</td>
<td>1·68</td>
<td>1675, 1625, 1285, 895</td>
</tr>
<tr>
<td>II</td>
<td>IX</td>
<td>VO(C₄H₆O₂N₅Cl₂)</td>
<td>8·21</td>
<td>13·32</td>
<td>1·70</td>
<td>1675, 1605, 1285, 890</td>
</tr>
<tr>
<td>III</td>
<td>X</td>
<td>VO(C₄H₆O₃N₅)₂</td>
<td>8·68</td>
<td>14·00</td>
<td>1·82</td>
<td>1670, 1612, 1275, 980</td>
</tr>
<tr>
<td>IV</td>
<td>XI</td>
<td>VO(C₄H₆N₅O₃)₉</td>
<td>8·21</td>
<td>12·39</td>
<td>1·77</td>
<td>1670, 1612, 1325, 950</td>
</tr>
<tr>
<td>V</td>
<td>XII</td>
<td>VO(C₄H₆O₃N₅)₉</td>
<td>8·69</td>
<td>14·20</td>
<td>1·79</td>
<td>1650, 1595, 1303, 960</td>
</tr>
<tr>
<td>VI</td>
<td>XIII</td>
<td>VO(C₄H₆O₃N₅Cl₂)</td>
<td>8·69</td>
<td>12·82</td>
<td>1·84</td>
<td>1650, 1610, 1295, 950</td>
</tr>
<tr>
<td>VII</td>
<td>XIV</td>
<td>VO(C₄H₆O₃N₅)₉</td>
<td>8·38</td>
<td>13·80</td>
<td>1·80</td>
<td>1640, 1612, 1290, 960</td>
</tr>
</tbody>
</table>

Values in parentheses are calculated ones.

**Physical Measurements.**—The conductance measurements in DMF were done on Philips PR 9500 conductivity bridge (cell constant 0·829 cm⁻¹).

The magnetic susceptibilities of the complexes at room temperature were determined on a Gouy balance using mercury cobalt thiocyanate as calibrant.

The infrared spectra of the ligands and the complexes in nujol mull were recorded on a Perkin-Elmer 337 spectrophotometer in the region 4000–650 cm⁻¹.

**Results and Discussion**

The complexes are dark brown in colour and are amorphous in nature. These are sparingly soluble in DMSO, DMF and pyridine. However the satisfactory electronic spectra were not obtained with solution. Limited solubility of these complexes in common organic solvents did not permit the determination of molecular weights.

The results of elemental analysis shown in Table I agree well with 1:2 stoichiometry. Oxovanadium (IV) sulphate loses its sulphate ion during the course of reaction with hydrazones. The proton of the o-hydroxy group is replaced by vanadium. The solution of these complexes in DMF do not show measurable conductance, hence the complexes are non-electrolytes.

**Magnetic Properties.**—The magnetic moments (Table I) corrected for the ligands determined for these complexes are in the range 1·68 to 1·84 B.M. This value is in close agreement with the values reported for oxovanadium (IV) containing one unpaired electron. It can be concluded that vanadium (IV) has not been oxidised to vanadium (V) state during the course of reaction.

**Infrared Spectra.**—The IR spectra are interpreted based on the previous assignments. In the
spectra of the ligands I–IV and V–VII medium intensity band observed in the region 3200–3170 cm\(^{-1}\) and 3130–3100 cm\(^{-1}\) respectively is assigned to NH stretching. The band observed in the region 2800–2700 cm\(^{-1}\) in ligands I–IV and 3480–3460 cm\(^{-1}\) in ligands V–VII is assigned to intramolecular hydrogen bonded OH. In the complexes the NH band is retailed but OH band disappears, indicating the replacement of H of hydroxy group by metal.

The strong band around 1675–1650 cm\(^{-1}\) (ν C = O) is present in ligands and is retained in the complexes. Three to four bands of medium to strong intensity are observed in the region 1625–1500 cm\(^{-1}\). These arise from various modes of vibration such as ν C=N, ν C=C, ν OH, δ N–H, etc., and their conclusive assignment is rather difficult. The band in the region 1625–1610 cm\(^{-1}\) is strong and shows a measurable shift to lower frequency by about 15–25 cm\(^{-1}\) in the complexes. Taking into consideration its intensity, the donor capacity of nitrogen and previous assignments\(^{1,8,9}\)

May reasonably be assigned to ν C=N and the shift may be due to the coordination of nitrogen to the metal. In the complexes IX, XI–XIV, the strong band observed around 960 cm\(^{-1}\) and in the complexes VIII and X the band around 890 cm\(^{-1}\) is assigned to ν C=O this probably suggests the monomeric nature of oxovanadium species\(^{12,18}\).

On the basis of above observations it may be concluded that ligands have reacted in keto form and vanadium has coordination number five in the above complexes. Generally five coordinate oxovanadium (IV) complexes have square pyramidal structures.


ANALYTICAL REACTIONS OF BARBITURIC ACIDS

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ABSTRACT

Analytical reactions of barbituric acids used in their identification and also the role of the acids as analytical reagents have been reviewed.

The name barbituric acid was given to the compound by Alfred von Baeyer who possibly discovered it on St. Barbara's day or wanted to honour his dear friend. It exists in the tautomeric forms I–III, though the X-ray studies\(^1\) of the solid favour the structure (III). Its preparation involves

$$\text{HO}$$

and the condensation of malonic acid with urea in the presence of POCl\(_3\). It melts at 248–252\(^o\) C (d).

Though the acid itself is not biologically active, substituents especially at 5–C atom make it so. Depressant activity of the compounds increases with heavier substituents. Also the compounds become rapidly more toxic when the molecular weights go beyond 250–300. The most commonly used barbiturates for medicinal purposes contain substituents with 6–10 C-atoms. In a recent article\(^2\) (incidentally one of the authors is Barbara) the biochemical and physiological aspects of barbiturates have been summarized. It is now proposed to review the subject from analytical standpoint.

Barbituric, thiobarbituric, diphenylbarbituric and diphenylchlorobarbituric acids have been used\(^3\) to quantitatively precipitate and estimate furfural. The method is superior to that using phloroglucinol. The