

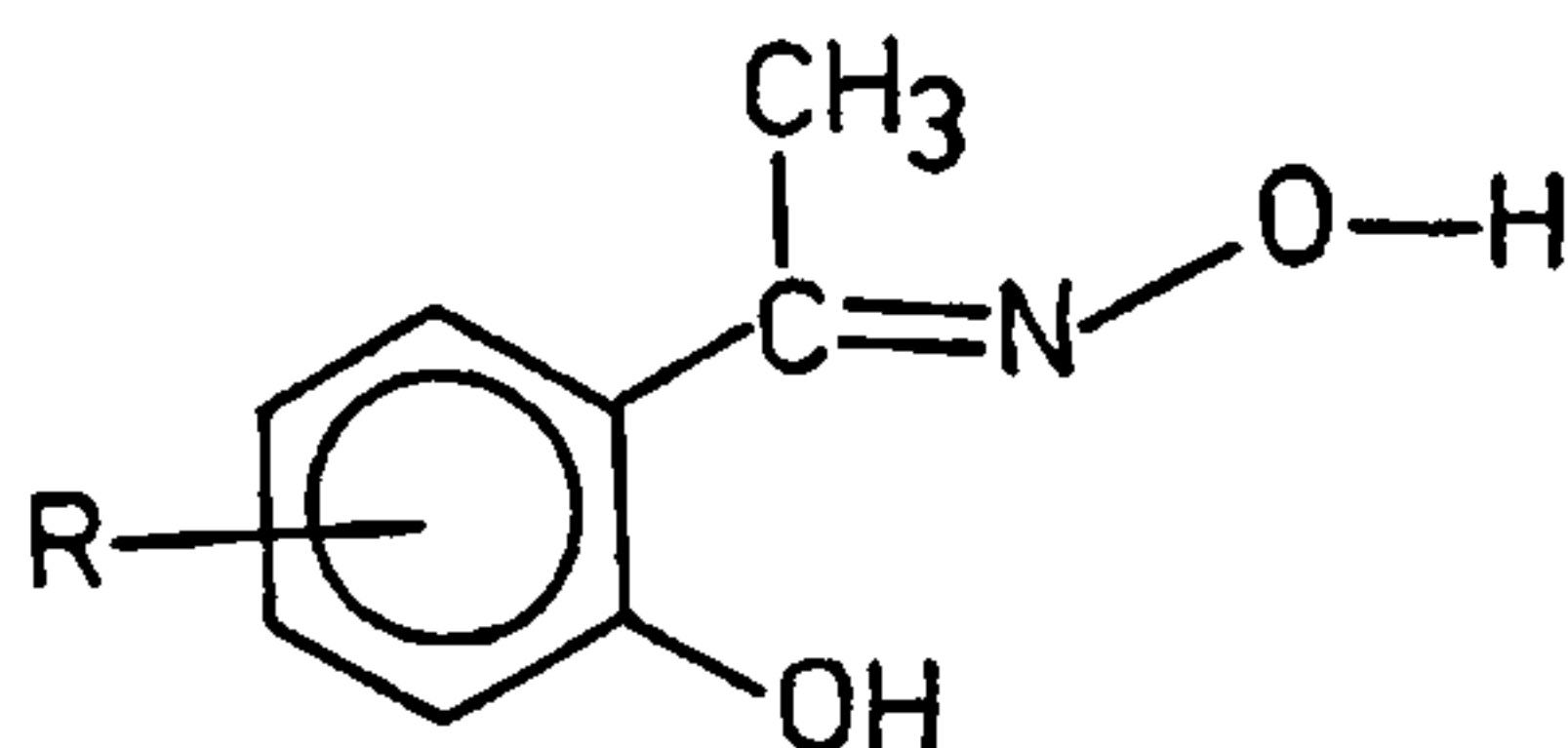
OXOVANADIUM(IV) COMPLEXES WITH *o*-HYDROXY ACETOPHENONE OXIMES

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THE oximes¹ are mainly used in analytical chemistry as organic reagents to precipitate many metals. Potentiometric study² on *o*-hydroxy acetophenone oximes with oxovanadium(IV) has been reported in the literature. Saksena³ *et al.*, have reported 2-OH-4 Me-5-Cl propiophenone oximes. Bielg and Mollinger⁴ have prepared the salicylaldoxime complexes of vanadium (IV) and (V). They have isolated the vanadium (IV) complex with composition $C_{14}H_{12}O_5N_2 V$ similar to ours.

The present series of investigations is to synthesize oxovanadium(IV) complexes with *o*-hydroxy acetophenone oximes and obtain structural information with the help of physicochemical methods. The oximes used are :



- R
- I. H
 - II. 3.Me
 - III. 4.Me
 - IV. 5 Me
 - V. 5 Cl

EXPERIMENTAL

Vanadyl chloride was of BDH make. The substituted *o*-hydroxy acetophenones were prepared according to the standard methods⁵. Hydroxylamine hydrochloride was of reagent grade. The oximes were prepared by heating 1 g. of *o*-hydroxy acetophenone, 1 g. of $NH_2OH \cdot HCl$ and 2 g. of sodium acetate in 10 ml. of ethanol on a steam bath for about an hour.

Vanadyl chloride (1 mole) in alcohol was treated with oximes (2 m mole) in the same solvent and refluxed for a while. The precipitated complex was filtered, washed with aq. alcohol and dried in vacuum over fused calcium chloride.

ELEMENTAL ANALYSIS

The vanadium and nitrogen in the complexes were estimated by conventional methods as pentoxide and by Kjeldahl method. C and H were estimated by microanalytical Department of Osmania University, Hyderabad.

RESULTS AND DISCUSSION

The analytical data given in Table I, shows that oxovanadium(IV) chloride forms complexes of 1 : 2 stoichiometry losing two of its chloride ions during the course of reaction. The molar conductance in DMF at 10^{-3} M are too small to account for any dissociation of the complexes in that solvent. The magnetic moment at room temperature (Table I) closely agrees with the spin only value of oxovanadium(IV) complexes hitherto reported⁶. Bielg and Mollinger⁴ reported a value of 1.70 B.M. for oxo-bis-(salicylaldoxime) vanadium(IV) complex.

ELECTRONIC SPECTRA

The electronic spectra of the complexes were taken with a Beckman DK-2 Spectrophotometer in chloroform in the region 300–900 nm. The electronic spectra of oxovanadium(IV) complexes are discussed in the literature⁷, in terms of C_{4v} and C_{2v} symmetry. The lowering of symmetry from C_{4v} to C_{2v} has the effect of removing the degeneracy in the *d*-orbitals and thus four transitions are predicted in the above region.

In the present investigation the spectra are all of similar pattern indicating that they have the same geometry. Out of the two distinct bands, the band around 490 nm is assigned to $d_{xy} - d_{x^2-y^2}$ transition. The broad intense maximum observed around 800 nm may be assigned to the $d_{xy} - d_{yz}, d_{xz}$ transition. We are less certain about the assignment of the third band in the high energy region which may be present as a tail of the charge transfer band.

INFRARED SPECTRA

The infrared spectra were taken in KBr pellets on Perkin Elmer-337, in the range 4000–400 cm^{-1} and the important frequencies are shown in Table I.

Comparison of the spectra of ligands with those of the complexes indicate bonding of oxygen of the

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TABLE I

Elemental analysis*, magnetic moment and important IR frequencies**

| Sl. No. | Complexes | % V | % N | % C | % H | μ_{eff} at room temp. | ν (OH) inter- and intra-molecular H-bonded | ν (C=N) | ν (C—O) | ν (V=O) |
|---------|---|------------------|----------------|------------------|----------------|----------------------------------|--|------------------|------------------|-------------|
| 1. | VO (2-OH-Acetophenone Oxime) ₂ | 13.51 (13.90) | 7.71 (7.63) | 52.28 (52.60) | 4.58 (4.38) | 1.65 | 3300s (3340s 2650b) | 1548s (1630s) | 1312s (1285s) | 992s |
| 2. | VO (2-OH-3Me-Acetophenone Oxime) ₂ | 13.12 (12.91) | 6.82 (7.08) | 55.22 (54.69) | 5.11 (5.06) | 1.60 | 3290 (3340s 2650b) | 1550s (1630s) | 1310s (1290s) | 990s |
| 3. | VO (2-OH-4Me-Acetophenone Oxime) ₂ | 12.90 (12.91) | 6.83 (7.08) | 55.51 (54.69) | 5.00 (5.06) | 1.72 | 3300 (3330s 2650b) | 1550s (1630s) | 1300s (1285s) | 995s |
| 4. | VO (2-OH-5Me-Acetophenone Oxime) ₂ | 12.46 (12.91) | 6.53 (7.08) | 55.46 (54.69) | 5.35 (5.06) | 1.65 | 3170s (3340s 2650b) | 1550s (1635s) | 1300s (1285s) | 988s |
| 5. | VO (2-OH-5Cl-Acetophenone Oxime) ₂ | 11.54 (12.23) | 6.35 (6.72) | 43.98 (43.93) | 3.15 (3.02) | 1.57 | 3220sb (3325s 2650b) | 1545s (1635s) | 1295s (1285s) | 998s |

* The values in parentheses are calculated values.

** The values in parentheses are for ligands.

OH group and nitrogen of the CH=N group⁸. Appearance of the intense band, in complexes around 980 cm⁻¹ indicates the monomeric nature of the complexes⁹.

All these observations indicate that these complexes have a coordination number of five. Generally five coordinate oxovanadium complexes have square pyramidal structure with oxygen at the apex.

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