



Synthesis, Characterisation and Structural Studies of Complexes containing Different Schiff Bases with V (III) and VO (IV)

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ABSTRACT

The Schiff bases 5-methyl-2-hydroxyacetophenone morpholine-N-thiohydrazide, 5-methyl-2-hydroxyacetophenone antipyrine, 5-chloro-2-hydroxyacetophenone morpholine-N-thiohydrazide has reacted with V(III) and VO(IV) to form co-ordination compounds having general formula $[V(C_{14}H_{19}O_2N_3S)3H_2O]Cl$;

$[VO(C_{14}H_{19}O_2N_3S)2H_2O]$, $[V(C_{20}H_{20}N_3O_2)_2]Cl$;

$[VO((C_{20}H_{20}N_3O_2)_2)]$; $[V(C_{14}H_{19}O_2N_3SCI)3H_2O]Cl$ and $[VO(C_{14}H_{19}O_2N_3SCI)2H_2O]$ respectively.

Where M=V (III) and VO (IV). The adducts have been characterized on the basis of elemental analyses molar conductance, I.R, visible spectra, magnetic susceptibility measurement and TGA. The ligands behave in dibasic tridentate manner in 5-methyl-2-hydroxyacetophenone morpholine-N-thiohydrazide and 5-chloro-2-hydroxyacetophenone morpholine-N-thiohydrazide. While 5-methyl-2-hydroxyacetophenone antipyrine behaves in monobasic tridentate manner. All these compounds are paramagnetic in nature and have octahedral geometry.

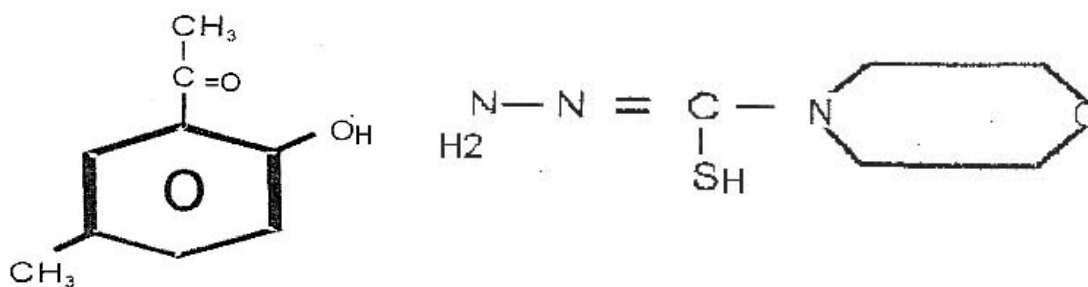
Key words: Coordination compounds, Molar conductance, Monobasic tridentate nature, Octahedral geometry and magnetic susceptibility.

INTRODUCTION

Compounds containing imines bases have not only found extensive application in organic synthesis, but several of these molecules display significant biological activity¹⁻⁴. In the last decade Schiff base ligands have received more attention mainly because of their wide application of in the field of catalysis and due to their antimicrobial⁵, antituberculosis⁶ and antitumour activity⁷. They easily form stable complexes with most transition metal ions. Hence Schiff bases are an important class of ligands in co-ordination chemistry and their

complexing ability containing different donor atoms is widely reported⁸⁻¹¹. The chemistry of Transition metal complexes containing heterocyclic donor continues to be on account of their biological importance¹²⁻¹⁴. Although vanadium has no role in the metabolism, yet its presence has been reported in lower as well as higher animals. It also finds several applications in many industrial processes to accelerate the reaction mechanism. It has been observed that Vanadium is used to inhibit cancer development in a variety of experimental animal models¹⁵ and it has a potential role in the fight against diabetes¹⁶.

The complexes of different Schiff bases (5-methyl 2- hydroxy acetophenone morpholine-N-thiohydrozone, 5- chloro 2-hydroxyacetophenone-morpholineNthiohydrazone and 5-methyl 2-hydroxy acetophenone antipyrine) with V (III) and VO (IV) have been synthesized in the lab. The structures of these complexes have been proposed on the basis of elemental analyses, electronic and IR spectral data and magnetic properties.



Scheme 1:

base. The metal salts used were $MnCl_2$ and $MnCl_3$ (Glaxo). Other chemicals like ethanol, methanol (Glaxo), DMF (Rankem), DMSO (Glaxo) etc were of highest purity and used as such.

The carbonyl compounds and amino compounds to be used are 5-methyl-2-hydroxyacetophenone and Morpholine-N-thiohydrazide. These compounds linked together to form azomethine linkage in the ligand (Schiff bases).

Infrared spectra and elemental analyses were carried out at CDRI (Lucknow). The magnetic susceptibility was measured by GOUY method. $CuSO_4 \cdot 5H_2O$ was used as calibrant. U.V-visible spectra were recorded with the help of Beckmans-DU at Chemistry Deptt. Bareilly College Bareilly. The conductivity measurement was carried out at room temperature and $10^{-3}M$ dilution using conductivity bridge model 910. The thermo gravimetric analysis was carried out at G.N.D. University Amritsar. Anti bacterial and anti fungal activities were carried out at IVRI Izzat Nagar Bareilly.

MATERIALS AND METHODS

The carbonyl compounds and the compounds of amino group used for the preparation of Schiff bases were of AR grade or equivalent purity. The carbonyl compounds (5-methyl-2-hydroxy acetophenone and 5-chloro-2-hydroxy acetophenone) and amino compounds (morpholine-N-thiohydrazide and 4-amino antipyrine) were used for the preparation of Schiff

EXPERIMENTAL

Preparation of ligands

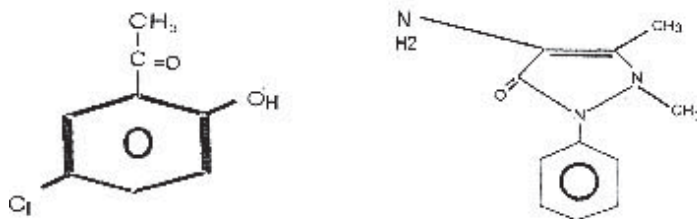
The Schiff bases were prepared by the condensation of Carbonyl compounds and compounds containing amino group. 1.41 gm of Morpholine N-Thiohydrazide was dissolved in Ethanol and refluxed on water bath for half an hour. Then 1.50 gm 5- methyl 2- hydroxy acetophenone was added to it and refluxed for about five hours. Similarly 2.06 gm of 4-Amino antipyrine was dissolved in methanol. The crystal of ligand so obtained was purified by recrystallization. The purity of crystal was checked by TLC and melting point. The ligands were characterized by elemental analysis, electronic and I-R spectra.

Preparation of complexes

All the metal complexes were synthesized by adding respective metal salts solution (vanadium chloride and oxovanadium sulphate) drop wise to the solution of the ligand (5- methyl 2- hydroxy acetophenone morpholine -N- thiohydrozone, 5- chloro 2 -hydroxy acetophenone morpholine N

thiohydrozone, 5-methyl 2-hydroxy acetophenone anti pyrine) prepared. The precipitate obtained was filtered and washed with suitable solvents (DMSO

and DMF) and dried in vacuum desiccator over fused P_4O_{10} .



Scheme 2: 5-chloro-2-hydroxyacetophenone and 4-aminoantipyrine were also used for the preparation of the ligands

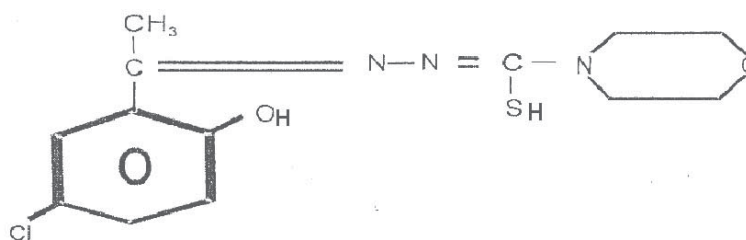
RESULTS AND DISCUSSION

The analytical data of 5-methyl 2-hydroxy acetophenone morpholine N thiohydrozone V (III) chloride complex and 5-methyl 2-hydroxy acetophenone morpholine N thiohydrozone VO(IV) complexes indicated 1/1 metal-ligands stoichiometry for the complex and hence the molecular formulae comes out to be $[V(C_{14}H_{19}O_2N_3S) 3H_2O]Cl$ and $[VO(C_{14}H_{19}O_2N_3S) 2H_2O]$ respectively. Similarly 5-chloro 2-hydroxy acetophenone morpholine N thiohydrozone V (III) chloride, 5-chloro 2-hydroxy acetophenone morpholine N thiohydrozone VO(IV) complexes also indicated M/L ratio 1/1. Hence molecular formulae of complex comes out to be $V(C_{14}H_{19}O_2N_3SCl)3H_2O]Cl$ and $[VO(C_{14}H_{19}O_2N_3SCl)2H_2O]$ respectively. The analytical data indicated 1:2 metal-ligand ratio for the 5-methyl-2-hydroxyacetophenoneantipyrineV(III)chloride complex and 5-methyl-2-hydroxyacetophenoneantipyrineVO(IV) complex. Hence the M.F formula of the adduct may be written as $[V(C_{20}H_{20}N_3O_2)_2]Cl$

and $[VO(C_{20}H_{20}N_3O_2)_2]$ respectively. The m.p of the metal complexes was found to be much higher than that of the ligand which indicated the formation of the adduct.

The values of molar conductance in DMF and DMSO AT 10^{-3} dilution and $250^\circ C$ indicated 1:1 electrolytic nature of 5-methyl 2-hydroxy acetophenone morpholine N-thiohydrozone V (III)chloride and 5-chloro 2-hydroxy acetophenone morpholine N-thiohydrozone V (III) chloride complex. While VO(IV) complexes of respective ligands were found to be non electrolytic in nature. 5-methyl 2-hydroxy acetophenone antipyrine V(III) chloride complex indicated 1:2 electrolytic nature and VO(IV) complex of respective ligand indicated non electrolytic nature of the complex.

The electronic spectra of V (III) complexes recorded in DMF, shows band at the range of $16600cm^{-1}$ $20000cm^{-1}$ which the shoulder at $19000cm^{-1}$ - $21700 cm^{-1}$ - which is assigned to ${}^3T_{1g} \rightarrow {}^3T_{2g}$ (16).



Scheme 3: 5-chloro-2-hydroxyacetophenone morpholine-N-thiohydrozone

The electronic spectra of VO(IV) complexes were also recorded in DMF, exhibited three bands at the range of 31600-33784 cm^{-1} , 20600-22900 cm^{-1} , 25840-25845 cm^{-1} corresponding to the charge transfer transitions and ${}^3T_{1g} \rightarrow {}^2E_g$. These are characteristics of octahedral oxo vanadium complexes¹⁸.

The IR spectra of complexes of 5-methyl 2-hydroxy acetophenone morpholine N thiohydrozone and 2-hydroxy 5-chloro acetophenone morpholine N thiohydrozone indicated di-basic tri-dentate nature of the ligand as revealed by the comparison of this spectrum with

that of the ligand shows band due to phenolic OH and $\nu_{C=S}$, which disappeared in the IR spectra of the complexes and a new band has appeared at the range of 745 to 760 cm^{-1} . This suggested the coordination of metal ion with the ligand through thiol-sulphur and phenolic oxygen via deprotonation. In addition to that the lowering of $\nu_{C=N}$ in the IR spectrum complexes by 15 to 20 cm^{-1} indicated the coordination of azomethine N, which is further substantiated by the appearance of azine chromophore at 1610 to 1615 cm^{-1} ¹⁸. This indicated that ligand is behaving in dibasic tridentate manner coordinating through oxygen, nitrogen and sulphur atoms.

Table 1: Characterisation of complexes prepared

S.No	Name of complexes M. Formula	C%	H%	N%	S%	M%
1.	5.Me2hyd.acet.mor.N.thV(III)chloride [V (C ₁₄ H ₁₉ O ₂ N ₃ S) 3H ₂ O]Cl	38.53	5.27	9.63	7.339	11.62
2.	5.Me2hyd.acet.mor.N.thVO(IV)complex [VO (C ₁₄ H ₁₉ O ₂ N ₃ S) 2H ₂ O]	36.9	5.11	9.61	7.21	12.722
3.	5.Me2hyd.acet.antipy.V(III)chloride [V (C ₂₀ H ₂₀ N ₃ O ₂) ₂] 2Cl;	63.49	5.55	11.11	-	6.754
4.	5.Me2hyd.acet.antipy.VO(III)complex [V (C ₂₀ H ₂₀ N ₃ O ₂) ₂]	65.12	5.69	11.39	-	6.938
5.	5.Chl.2hyd.acet.mor.N.thV(III)chloride [V (C ₁₃ H ₁₄ N ₃ O ₂ SCl).3H ₂ O] Cl	34.51	4.42	9.29	7.07	11.30
6.	5.Chl.2hyd.acet.mor.N.thVO(IV)chloride [VO (C ₁₃ H ₁₄ N ₃ O ₂ SCl).2H ₂ O]	37.68	4.83	10.14	7.72	12.31

Table 2:

S.No	Name of complex	Magnetic moment (B.M)	Melting Point(°C)
1.	5.Me2hyd.acet.mor.N.thV(III)chloride [V (C ₁₄ H ₁₉ O ₂ N ₃ S) 3H ₂ O]Cl	2.89	330
2.	5.Me2hyd.acet.mor.N.thVO(IV)complex [VO (C ₁₄ H ₁₉ O ₂ N ₃ S) 2H ₂ O]	1.70	326
3.	5.Me2hyd.acet.antipy.V(III)chloride [V (C ₂₀ H ₂₀ N ₃ O ₂) ₂] 2Cl;	2.83	376
4.	5.Me2hyd.acet.antipy.VO(III)complex [V (C ₂₀ H ₂₀ N ₃ O ₂) ₂]	1.73	380
5.	5.Chl.2hyd.acet.mor.N.thV(III)chloride [V (C ₁₃ H ₁₄ N ₃ O ₂ SCl).3H ₂ O] Cl	2.84	342
6.	5.Chl.2hyd.acet.mor.N.thVO(IV)chloride [VO (C ₁₃ H ₁₄ N ₃ O ₂ SCl).2H ₂ O]	1.69	320

The IR spectrum of the complexes exhibited some new bands. The band at 3100 to 3480 cm^{-1} may be attributed to νOH of coordinated water. This is further supported by the band at 810 to 880 cm^{-1} may be due to rocking & wagging modes of coordinated water molecules²⁰⁻²¹.

This inference of IR spectrum regarding the presence of coordinating water molecule is further supported by TGA. The thermogram shows the loss of three water molecules above 150 to 170°C. In the far IR region two bands were observed at the range of 400 to 480 & 500 to 590 cm^{-1} which may be assigned to $\nu\text{M-N}$ & $\nu\text{M-O}$ vibrations respectively²².

The I.R. spectra of the complexes displayed V=O frequency at 940 cm^{-1} which is compatible with 6 co-ordination²²⁻²³.

The I.R. spectra of the complexes of 5-methyl-2-hydroxyacetophenoneantipyrine on comparison with that of ligands indicated coordination through cyclic C=O , phenolic oxygen and azomethine nitrogen. This indicated monobasic tridentate nature of the ligand. The band due to νOH present at 3500 cm^{-1} which disappeared on complexation and appearance of new band at 1250 to 1270 cm^{-1} which indicated the bonding of ionized phenolic oxygen to the metal ion²⁴. The strong band at 1590 cm^{-1} characteristics of the azomethine group in the free Schiff base has shifted to lower frequency of 1560-1570 cm^{-1} in the complexes indicating that

azomethine N is one of the co-coordinating atoms in Schiff base.

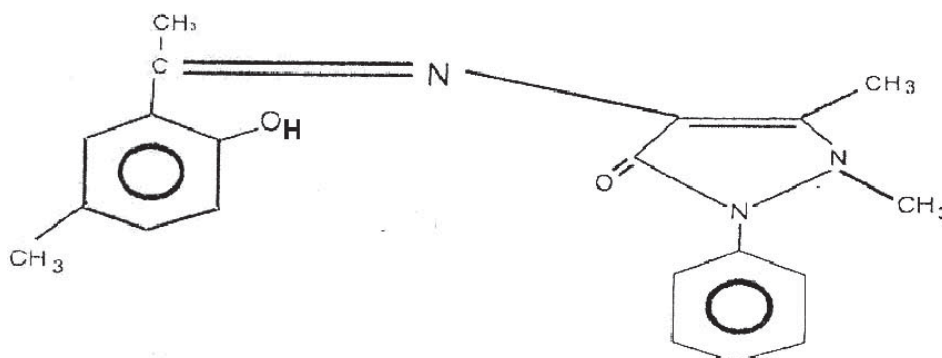
The band observed at 1656 cm^{-1} characteristics of the cyclic carbonyl group of the pyrazolone ring of free Schiff base has shifted to lower frequency in the i.r range of 1610-1620 cm^{-1} in the complexes, indicated the coordination of the above group with metal ion(24). This is further supported by the formation of new bands in i.r spectrum of the complex at 460-475 cm^{-1} and 410-415 cm^{-1} . Which are due to $\delta\text{M-O}$ and $\delta\text{M-N}$ bands respectively .

Biological studies

The ligands and the complexes were screened for antibacterial and antifungal activities. The antifungal activity was done against *Macrophomia Phaseolina* and *Fusarium oxysporum* using a procedure using for testing new chemicals²⁶.

The linear growth of the fungus was recorded by measuring their diameter of the fungus colony after 96 hours and the percentage inhibition was calculated by the formula $100 \times (d_c - d_t) / d_c$ where d_c and d_t are the diameters of fungus colony in the control and the test plates respectively.

Antibacterial activity was tested against *Bacillus subtilis* and *Salmonella* species using the paper disc plate method²⁷.



Scheme 5: 5-methyl-2-hydroxyacetophenoneantipyrine (azomethine linkage (C=N)

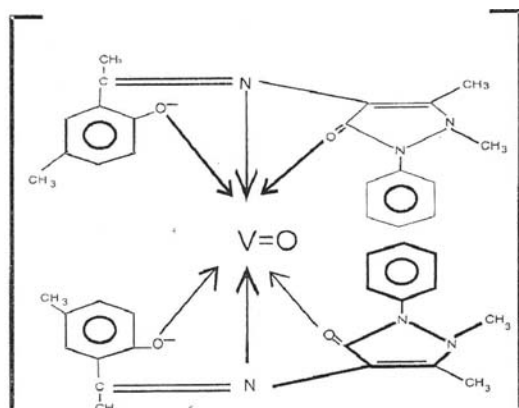


Fig. 1: 5-Methyl 2-hydroxyacetophenone antipyrineoxovanadium complex

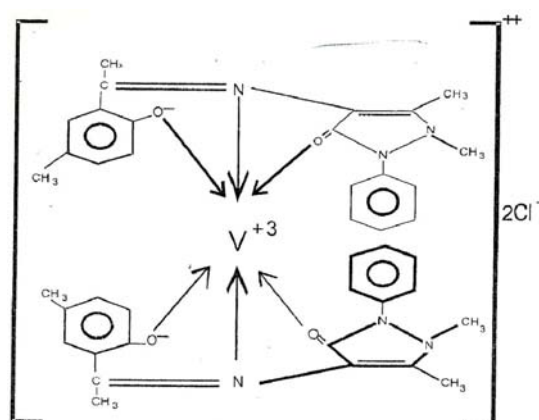


Fig. 2: 5-Methyl 2-hydroxyacetophenone antipyrinevanadium chloride complex

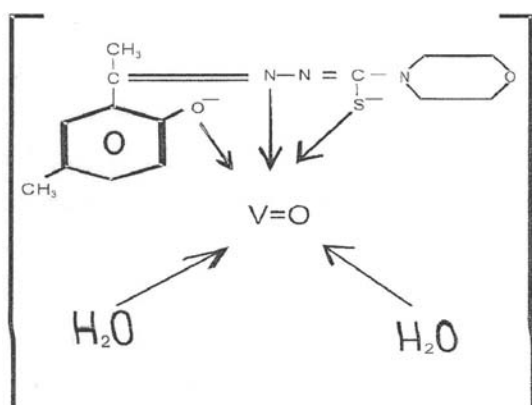


Fig. 3: 5-Methyl 2-hydroxyacetophenone morpholine-N-thiohydrazoneoxovanadium complex

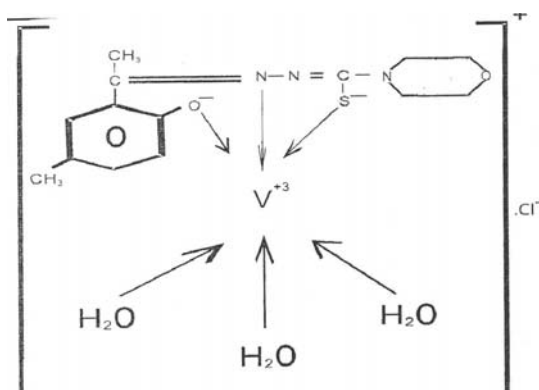


Fig. 4: 5-Methyl 2-hydroxyacetophenone morpholine-N-thiohydrazonevanadium chloride complex

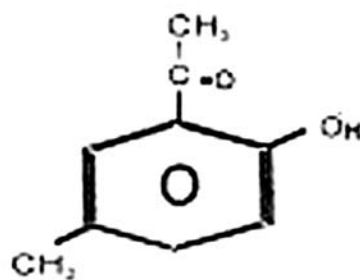
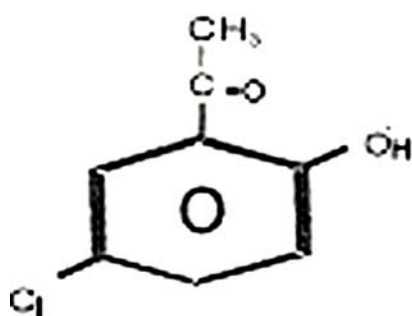


Fig. 5: 5-chloro-2-hydroxyacetophenone & 5-methyl-2-hydroxyacetophenone

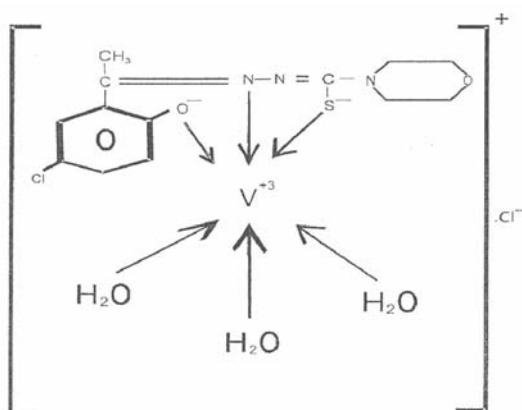


Fig. 7: 5-chloro-2-hydroxyacetophenemorpholine-N-thiohydrazonevanadium chloride complex

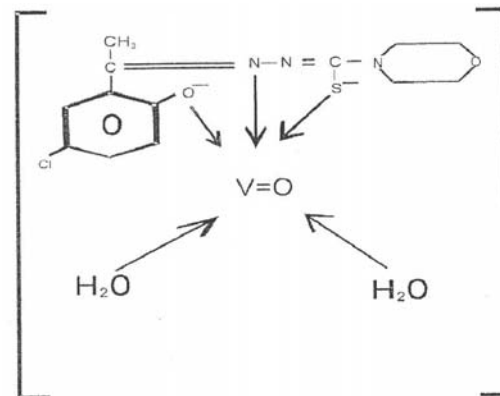


Fig. 8: 5-chloro-2-hydroxyacetophenemorpholine-N-thiohydrazoneoxovanadium complex

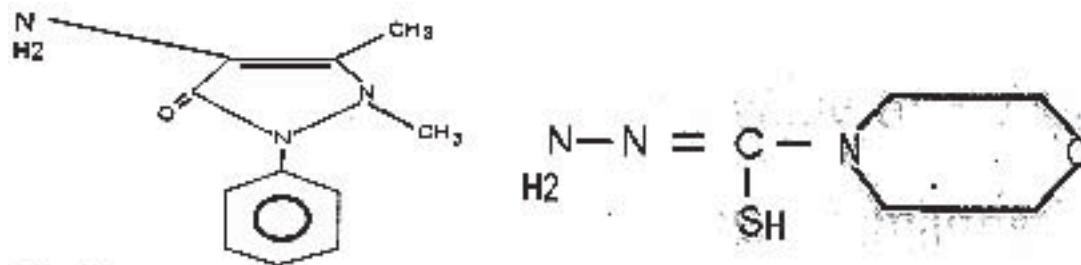


Fig. 9: Amino Compounds (4-aminoantipyrine and Morpholine-N-thiohydrazone) are found to be biologically potent

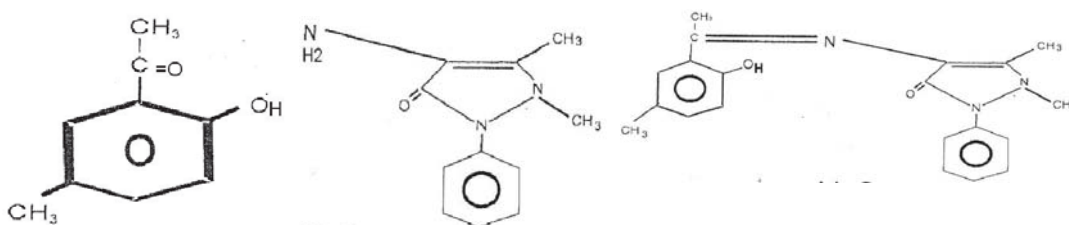
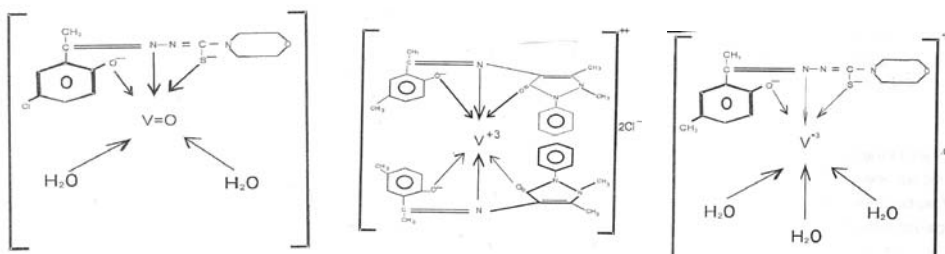


Fig. 10: The ligand(5-methyl-2-hydroxyacetophenoneantipyrine) is formed by dehydration of amino and carbonyl compounds



Hence complexes are obtained by using many amino and carbonyl compounds with V(III) and VO(IV)

CONCLUSION

On the basis of above mentioned facts the complexes may be tentatively assigned the octahedral geometry which were found biologically active.

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