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A Comprehensive Analysis of Vanadium (III) and Its Complexes With Schiff Bases

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Abstract
Vanadium is the third member of first transition series and have five valency electrons. Its oxidation states varies from (IV) to -(I). Vanadium (III) complexes are usually prepared from vanadium (V) or vanadium (IV) by electrolytic reduction, few vanadium (III) complexes were prepared by using VCl_3 *as starting material. Usually, vanadium (III) complexes are unstable towards air or moisture and have to be prepared under an inert atmos. The most common co-ordination number of vanadium is six having octahedral geometry for all the oxidation states of metal. While few vanadium (III) complex compounds are known in which the co-ordination is four, five or seven consisting tetrahedral, trigonal bipyramidal or pentagonal geometry around the vanadium (III) ion. This paper comprises studies of vanadium (III) complexes (consisting* d^2 *system) with some schiff base ligands such as: bis (*p^-*-methoxy benzaldehyde) Sulphonamide,* p^-*-methoxy benzaldehyde sulphafurazole,* p^-*-methoxy benzaldehyde sulphisomedine, bis (N,N'-Di methyl-4-amino benzaldehyde) sulphonamide, N,N'-Dimethyl-4-amino benzaldehyde sulphafurazole, N,N'-Di methyl-4-amino benzaldehyde sulphisomedine, bis (N,N'-Di methyl4-amino cinnamaldehyde) sulphonamide, N,N'-Dimethyl-4-amino cinnamaldehyde sulphafurazole and N,N'-Dimethyl-4-amino cinnamaldehyde sulphisomedine. The vanadium tri chloride was used of Analar grade (BDH England) for the preparation of vanadium (III) complexes.*

Keywords: *Vanadium complex compounds , Schiff base, co-ordinate compounds.*

I. Introduction

The element Vanadium was recognised in 1831, when N.G. Sefstrom was able to isolate and characterize the oxide; the name vanadium was derived from vanadis. The beautiful colour of vanadium compound had been observed as early as 1801, by A.M. Rio in his experiments with a new element he called erythronium because of the red colour after treatment with acid (1).

There are vanadium compounds with formal oxidation states from 3 upto +5 with the exception of -2, under the ordinary conditions, the most stable state are +4. Suitable sources of information from the early chemistry of Vanadium are Mellor's (2) and Sidgwick (3) books. More recent work is covered by several reviews (4-8). The co-ordination chemistry of vanadium is strongly influenced by the oxidizing/reducing properties of the metallic centre, and the chemistry of vanadium ion in aqueous solution is limited to oxidation states +2, +3, +4, & +5, although V^{+2}can reduce water.

Although many vanadium (III) complexes are unstable in air, there are quite a few compound in this oxidation state, most with octahedral geometry. However, remarkable seven coordinate complexes were also characterized. Vanadium (III) ions are part of the respiratory pigment has been ruled out recently.

The +4 oxidation state is the most stable under ordinary conditions and the majority of vanadium (IV) compound contain the VO^{+2} unit (Vanadyl ion), which can persist through a variety of reactions. Its complexes typically have square pyramidal or bipyramidal geometry with the vanadyl oxygen apical and the v-atom lying above the plane defined by the equatorial ligand. Trigonal bipyramidal complexes are also known.

Many vanadyl complexes are not air stable and generally they can be easily hydrolysed and/or oxidised to the +5 oxidation state.

V (III) compound are usually prepared from $V^{(V)}$ or $V^{(IV)}$ by electrolytic reduction; many complexes were prepared using VCl_3 as starting material. Usually, vanadium complexes are unstable towards air or moisture and have to be prepared under an inert atmosphere. Many have octahedral co-ordination and their electronic spectra are typical of a^2 ions with three spin-allowed d-d transitions

$$y_1 = {}^3T_{2g}\ (F) \leftarrow {}^3T_{ig}\ (F)$$

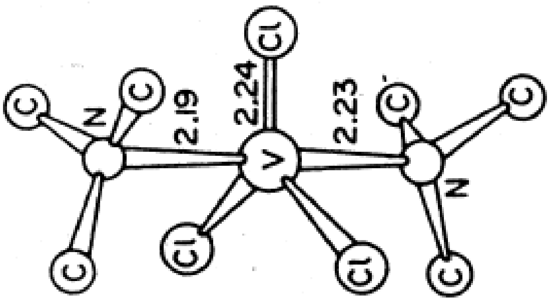
$$y_2 = {}^3T_{ig}\ (P) \leftarrow {}^3T_{ig}\ (F)$$

$$y_3 = {}^3A_{2g}\ (F) \leftarrow {}^3T_{ig}\ (F)$$

Usually, the third band is not observed as it is weak and frequently masked by charge-transfer transitions. Several procedures for the preparation of cyanide complexes have been reported. The hepta cyanovanadate (III) ion has been shown to be a pentagonal bipyramidal from a crystalographic study of $K_4V(CN)_7.2H_20$ (8 & 9). A monohydrate (10) of $K_4(V(CN)_7)$ and the preparation of the anhydrous material have also been reported (11). Thegeometry of the anions in all cases has been suggested to be the same (12). The Infra-Red spectrum of dihydrate shows two bands (2100 and 2070 cm^{-1} similar to those in solution (2104 & 2027 cm^{-1}). Therefore, the anion in solution must be $(V(CN)_7]^{-4}$with a pentagonal bipyramidal geometry. On reaction of ammonia with vanadium (III) halides there is ammonolysis of one V-X bond. The amidohalides $VX_2(NH_2)$. nNH_3 (X = Cl (12 & 13) or Br (14,15) n=4-5 have an ammonia content that depends on the temperature. A similar compound $V(NCS)_2(NH_2)^{\cdot}4NH_3$ has been prepared from $V(NCS)_3$ in THF with NH_3 (16). VCl_3 with primary amines gave similar derivatives containing one co-ordinated amide and one or more molecules of amine (17), but ethylenediamine (18 & 19) and propylenediamine (20) give $[V(L)_3]Cl_3$ (L = en, py).

Tetrahedral blue-black compound $[VL_4](SCN)_3$ (L = en or Me_4en) were prepared (21) from $K_3[V(NCS)_6]$ and their electronic spectra are comparable to other tetrahedral vanadium (III) complexes with substituted pyridines. Their spectra have been studied (22), e.g. $[V(py)_4](NCS)_3$ has three bands at 9500, 16200 and 25000 cm^{-1} assigned as ${}^3A_2{}^3T_{2,}{}^3A_2{}^3T_1$, (F) and ${}^3A_2{}^3T_1$ (P).

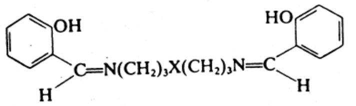
On reacting vanadium (IV) chloride or vanadium (III) bromide with trimethylamine VX_3 $(NMe_3)_2$ (X=Cl or Br) were obtained (23). The driving force for the reduction of $[VCl_4]$ is the formation of $VCl_3(NMe_3)$ (24). This chocolate brown compound has been isolated from the solution remaining after extraction of the pink-mauve $[VCl_3(NMe_3)_2]$ whose structure has been determined and have a trigonal bipyramidal geometry (25).



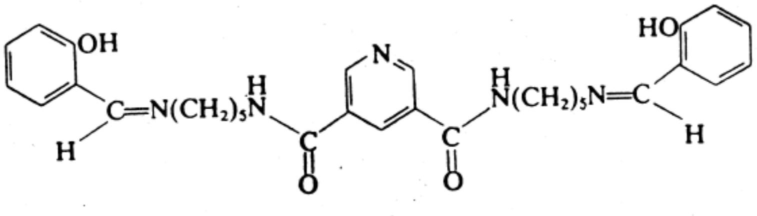
$VCl_3(Py)_3$ has been prepared (26 & 30) and binding energies measured by ESCA (31). A similar preparative procedure was used to isolate tetrahedral complexes of bidentate donors (L = bipy or phen) $[VL_2](SCN)_3$. However, complexes of vanadium (III) chloride' or bromide with these same bidentate donors have stoichiometri depending on conditions (32).

From spectroscopy, the formation constant $V(NCS)^{+2}$ is 10^2 (33). Complexes containing $[V(NCS)_6]^{-3}$ have been isolated and the structure of $K_3[V(NCS)_6].12H_20$ determined by X-ray diffraction (34) confirming that thiocyanate co-ordinate via the N-atom (the mean V-N distance in this complexes is 2.044 (2) Å).

VCl_3in acetonitrile reacts with ammonia thiocynate, a progressive exchange occurs (35). Complexes with various stoichiometric were isolated: $VCl_2(NCS)$.3MeCN,$VCl(NCS)_2$. 3MeCN, $V(NCS)_3$.5MeCN and $Cl_3[V(NCS)_6]^{\cdot}2MeCN(Ct=K^+$, NH_4^+,PyH^+). Salen to reacts with vanadiun trichloride in pyridine under high hurity nitrogen, a brown solid formulated as [VCl(Salen)(Py)] precipitated. The geometry is probably octahedral with Cl^- and py. trans. Conductance showed it to be a 1:1 electrolytic nature for complex. Complexes with shiff base beyond (a) and (b) and with the structurally related (c) have been prepared by adding the THF adducts of VCl_3 to solution of the corresponding ligands, . They are monomers [VCl(SB)](SB = Schiff base (a-c). I.R. indicates co-ordination through phenolic oxygen and azomethine nitrogen and magnetic moments found to be 2.5 to 2.7 B.M.; are consistent with pseudo-octahedral $V.^{(111)}$ (36).

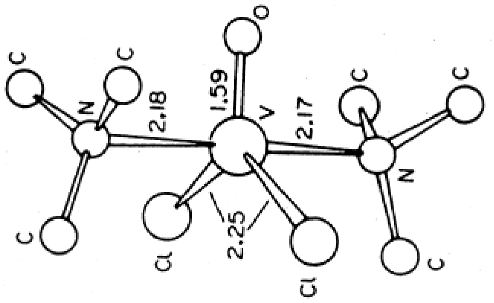


(a) X = N
(b) X = P

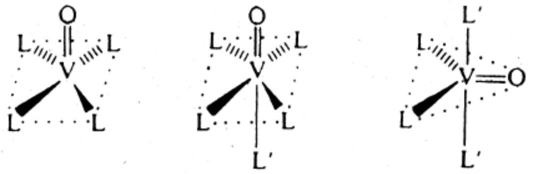


(c)

V (IV) oxidation state is the most stable under ordinary conditions (37). Important compounds contain the VO^{+2} unit (Vanadyl (IV) ion or oxovanadium (IV). ion), which can persist through a variety of reaction and considered the most stable oxycation of the row transition ions (38) It forms stable anionic, cationic and neutral complexes with all type of ligands and has one co-ordir ation position occupied by the vanadyl oxygen.



The complexes typically have square pyramidal or bipyramidal structure with vanadyl oxygen apical, the vanadium atom lying 0.035-0.055 A above the plane defined by the equatorial ligands (38). There have been reports of five co-ordinate 'trigonal bipyramidal' complexes with structures determined by X-ray diffraction techniques. Only three general review on vanadium (IV) complexes have been given. (39 & 40).

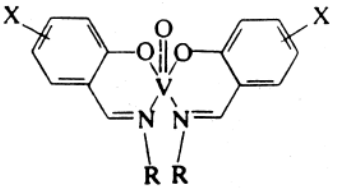


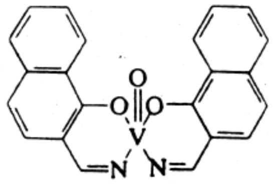
Complexes [$VOCl_2L_n$] (L = monodentate and bidentate netural ligands; n = 1, 2 or 3) are made by method including controlled hydrolysis of vanadium(IV) chloride adducts (41,42) controlled oxidation of vanadium(III) chloride adducts (43, 44) reaction of ligand with aqueous $VOCl_2$, (45,46) with $VOCl_3$ (47,48) or with $VOCl_2(MeOH)_3$ in methanol (49).

The chloride of [$VCl_{4]}$ may be substituted by amide with primary and secondary amines at room temperature, aminolysis stop at the dichlorodiamides. Ethylenedianine oxovanadium (IV) complexes in water have been reported (50) and dark brown $[V(en)_3]F_4$ has been prepared by adding VF_5 to the diamine at low temperature (51).

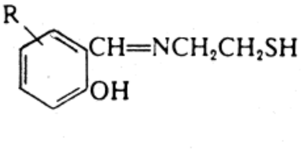
Vanadium (IV) complexes with Schiff based derived from the reaction of diamines and salicylaldehyde and derivatives have been reported. The complexes with schiff bases derived from diamines and salicylaldehyde normally have 1:1 stoichiometry.

Most of compounds with schiff bases have been reported by Gmelins Handbuch (40). Preparation consists simply in adding an aqueous-alcoholic [EtOH or MeOH] solutin of the corresponding amine and $NaMeCo_2$ to an alcoholic solution of $VOCl_2$ or ($VOSO_4$) and the salicylaldehyde derivatives. The complexes are often purified by recrystallisation from ethanol. Compounds are brownish grey-green and complexes are green (52). They are soluble in $CHCl_3$ and CH_2CL_2 but less soluble in methanol, ethanol & benzene. These complex show electronic spectra in pyridine with one different from the spectra of the same complexes in the solid state and in chloroform, this indicates in pyridine, six coordinate solvates:

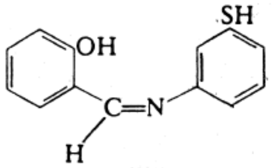




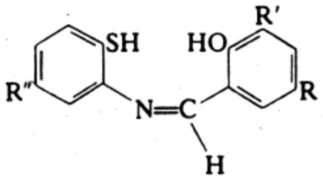
Oxovanadium (IV) complexes with schiff base derived from Hsalor substituted Hsal and 2-aminoethanethiol and 3-aminothiophenol were prepared by Syamal (53). These ligand behave (Fig. I&II) as bidentate monobasic ligands and forms complexes (Fig. I&II) $[VO(SB)_2]$, a square pyramidal structure was suggested with co-ordination through oxygen atom and nitrogen of the azomethine group



(I)



(II)



PREPARATION OF VANADIUM (III) COMPLEXES

Vanadium (III) complexes were synthesised by the addition of vanadium tri chloride solution in methanol to the THF solution of schff base ligands in the atmosphere of nitrogen. The precipitate thus, obtained was washed with THF and dried in vacuum desiccator over anhydrous calcium chloride. These complexes were subjected to elemental analysis and melting points were determined. They were also subjected to TGA, infra red spectral studies, conductivity measurements and magnetic properties were also studied.

II. RESULTS AND DISCUSSION

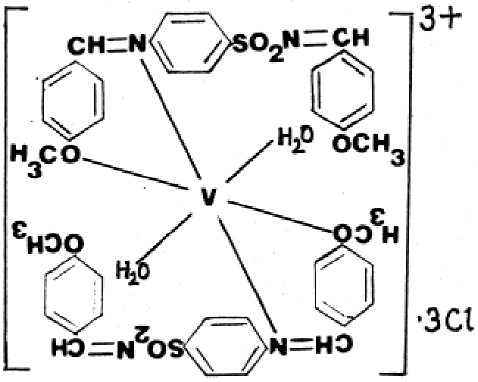
bis(p-methoxy benzaldehyde) Sulphonamide Vanadium(III) Chloride

The elemental analysis indicates that vanadium (III) chloride reacts with bis (p^- -methoxy benzaldehyde) sulphonamide in the molar ratio of 1:2 to give pink coloured adduct. The composition of complex has been found to be $[(C_{22}H_{20}N_{2,}O_4S)_2\ 2H_20\ VC1_3]$. The melting point of the ligand is 180°C and that of the complex was 279°C, which indicates that a new complex compound has been formed. The molar conductance of the complex in three solvents, methanol, DMF and DMSO at 0.001 molar concentration comes to be 360.0, 324.0 and 298,6 $Ohm^{-1}\ cm^2\ mo1^{-1}$, respectively, which indicates the 1:3 electrolytic nature of the complex. The magnetic moments of the complex at room temperature were found to be 2.80 B.M., which is quite close to the expected value of 2.83 B.M. as calculated for d^2 system. It means vanadium (III) ion has not been oxidised on complexation.

The IR spectra of the ligand shows some important absorption peaks at 2885(m), 2800(m), 1670(w), 1610(s), 1340(w) and 1175(s) cms^{-1} These may be attributed to γC-N, γC-H vibration in aromatic ring, C=0 stretching, C=N stretching vibration, γC aromatic N vibration and γC aromatic Oaromatic vibrations, respectively. The spectra of the complex shows broad and weak absorption peak at 3420(bw) cm^{-1} due to 0-H vibration, in addition to it few important bands appears at 2800(w) cm^{-1} (CH)- vibration 1680{w} cm^{-1} (C=0), while γ(C=N) vibrations appears at 1600(vs) cm^{-1} suggesting co-ordination through nitrogen of azomethine group. It also shows, a lowering in frequency for γCaromatic Oaromatic Cvibrations, which appears at 1150(vs)cm^{-1} suggesting involvement of methoxy oxygen in co-ordination. But other absorption bands appeared without deviations. A new absorption b and appears in the spectra of the complex at 940(s) cm^{-1} is due to co-ordinated water molecules, which is also supported by TGA studies.

In this way, schiff base ligandis acting as a bidentate ligand. The metal ion is hexa co-ordinated and should have octahedral geometry (179) around the V (III) ion.

Proposed structure of the complex is-

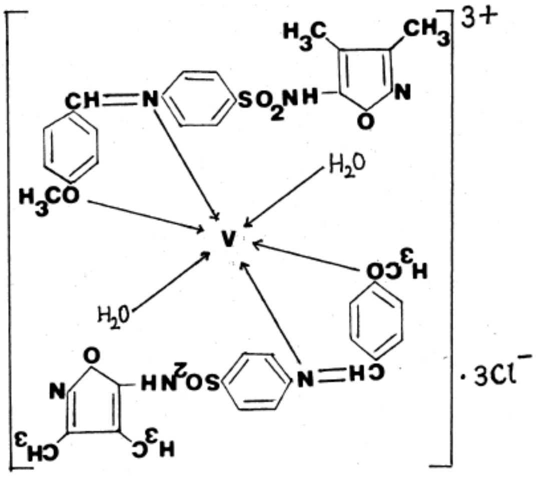


p$^-$ -methoxy benzaldehyde Sulphafurazole Vanadium (III) Chloride

On the basis of elemental analysis for carbon, hydrogen, nitrogen, chlorine, and metal, the composition of the vanadium (III) complex is $[(C_{19}H_{19}N_3O_4S)_2\ 2H_20\ VC1_3)$. This establishes 1:2 metal-ligand stoichiometry. It is a buff coloured adduct, which shows the sharp melting point at 156°C. The melting point of schiff base ligand was observed as 108°C, this indicates that a new complex compound has been formed. The molar conductance of the complex in three solvents viz., methanol, DMF and DMSO at 0.001 molar concentration were found to be 331.0, 298.4 and 307.0 Ohm^{-1} cm^{2}mo1^{-1}respectively, which are indicative of 1:3 electrolytic nature of the complex. The value of magnetic moment for the complex has been found to be 2.81 B.M., indicating its paramagnetic nature. The observed μ_{eff} is quite close to the spin only value for two unpaired electrons.

The IR spectra of the ligand shows some significant absorption peaks at 2920(w), 2805(w), 1660(m), 1600(s), 1350{w} and 1135(s) cms^{-1} which may be assigned to γ C-N, γ C-H vibration in aromatic ring, C=O stretching, HC=N stretching vibration, γCaromaticN vibration and γCaromaticOaromatic aliphatic vibrations, respectively. The spectra of the complex also shows a number of absorption peaks, a few of them showing shifts to 1620(vs) cm^{-1} and 1125(vs) cm^{-1}. This suggests that nitrogen of azomethine group and oxygen of methoxy group are participating in coordination. A new peak appears at 920 (m) cm^{-1} in the spectra of the complex. This may be due the presence of co-ordinated water molecules. Thus, the schiff base molecule seems to be acting as a bidentate ligand.

It, therefore, appears that the out of six coordination sites two are occupied by water molecules and four by two bidentate ligand molecules. Hence, complex appears to possess octahedral geometry around the central metal ion. Proposed structure of the complex is-



p$^-$-methoxy benzaldehyde Sulphisomedine Vanadium (III) Chloride

The composition of red-brown coloured complex on the basis of elemental analysis for carbon, hydrogen nitrogen, chlorine and metal is established as $[(C_{20}\ H_{20}\ N_4\ O_3\ S)_2.\ 2H_20\ VCl_3\ ]$, which indicates 1:2 metal-ligand ratio in this adducts. The melting point of the schiff base ligand is 155°C and that of the complex has 213°C. It indicates that a new complex compound has been formed. The molar conductance of this adduct in three solvents viz., methanol, DMF and DMSO at 0.001 molar concentration were found to be 328.0, 796.6 and

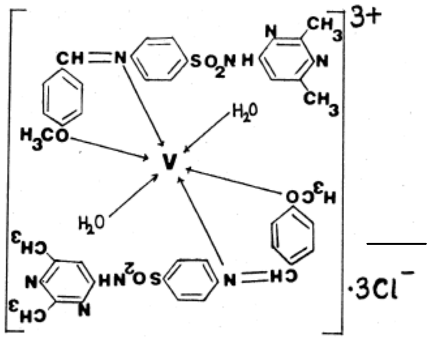
299.4 Ohm^{-1}cm^{2}mol^{-1}, respectively. The values of molar conductance suggested 1:3 electrolytic nature of the complex.

The magnetic moments of the complex at room temperature were found to be 2.75 B.M, The value is slightly lower than the expected value for two unpaired electrons. The IR spectra of ligand shows some important absorption bands at 3230(w), 2800(w). 1665(m), 1620(s), 1355(w) and 1130(m) cms^{-1}, which may be attributed to γ (N-H), γ (C-H) vibration in aromatic ring, C=O' stretching, HC=N stretching vibration, γCaromatic N$_{\text{vibrations}}$ and γCaromatic O aromatic Cvibrations, respectively.

The spectra of the complex exhibit broad and weak peak at 3410(bw) cm^{-1} due to γO-H vibration in addition to few important bands at 2835(w) cm^{-1}γ(C-H vibrati~~on),~~ 1670~~(m)~~ cm^{-1} (C=0~~ vibra~~tion). ~~Howe~~ver, γ C=N vibration occurs at 1640(vs) cm^{-1} suggesting co-ordination through nitrogen of azomethine group. It also shows a shifting at Caromatic-OaliphaticC vibrations which appeared at 1145(s) cm^{-1} indicating the participation of methoxy oxygen in co-ordination. But other absorption peaks appeared without or with slight deviations.

A new absorption band appears at 920(m) cm^{-1} is due to co-ordinated water molecules. Thus, the schiff base ligand acting as a bidentate ligand. It, therefore, appears that the out of six coordination sites four are occupied by two bidentate ligand molecules and two sites by two water molecules. Therefore, vanadium (III) complex seems to be octahedral geometry around the central metal ion.

Proposed structure of the complex is

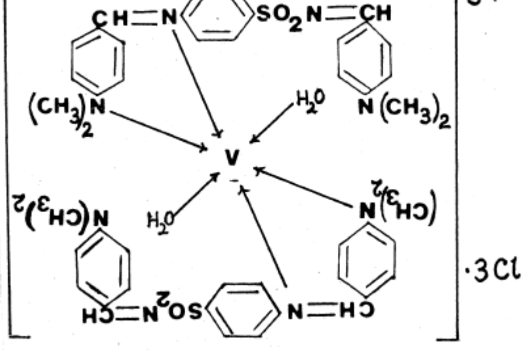


bis (N,N'-Dimethyl-4-amino benzaldehyde) Sulphonamide Vanadium (III) Chloride

The elemental analysis indicates that vanadium tri chloride reacts with bis (N,N'-dimethyl-4-amino benzaldehyde) sulphonamide in the stoichiometry ratio of 1:2. The melting point of the ligand is 198°C, and that of the complex is 261°C. It indicates that a new complex compound has been formed. The molar conductance of the complex in three solvents viz., methanol, DMF and DMSO in 0.001 molar concentration shows its 1:3 electrolytic nature.

The IR spectra of the ligand exhibits some important absorption bands at 1620(s), 1640(s) and 1140(m) cms^{-1}, which have been shifted to 1625(vs), 1645(vs) and 1150(s) cms^{-1} in the spectra of the complex, respectively. This indicate that the coordination have taken place through nitrogen of azomethine and the nitrogen of substituted amino group [-N(CH$_3$)$_2$]. Thus, the ligand is acting as a bidentate. In this way, six co-ordination sites in the complex are occupied by two ligand molecules and two by water molecules. This is supported by a sharp peak at 730 cm^{-1} in the spectra of the complex. This is also supported by the TGA studies. Similar conclusions have been drawn by other workers in this field (15). The complex appears to have octahedral shape. The magnetic moments of the complex at room temperature were found to be 2.71 B.M., which is slightly lower than the expected spin only value for d^2 system i.e. 2.83 B.M.

Proposed structure of the complex is-

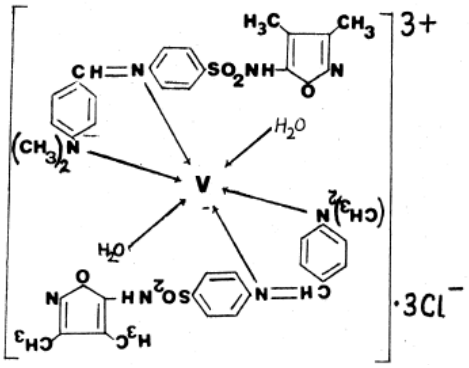


N,N'-Dimethyl-4-aminobenzaldehyde Sulphafurazole Vanadium(III) Chloride

The analytical data of this complex indicates that two molecules of schiff base ligand have reacted with vanadium (III) chloride ion. The composition of the complex is, therefore, $[(C_{20}H_{22}N_4O_3S)_2,2H_2O\ VC1_3)$. The complex thus, obtained is of orange colour and has a melting point of 287°C, whereas that of the ligand was found to be 200°C. It appears that a new complex compound has been formed. The magnetic moment of the complex was found to be 2.67 B.M., which is slightly lower than the expected value for do system i.e. 2.83 B.M. The lower value of magnetic moment may be due to lower symmetry and higher orbital contribution.

The molar conductance of the complex in the three solvents, i.e. methanol, DMF and DMSO at 0.001 molar concentrations were found to be 369.7, 335.7 and 298.1 Ohm^{-1} cm^2 mol^{-1} at room temperature, respectively. These values of molar conductance suggest 1:3 electrolytic nature of the complex. The IR spectrum of the schiff base ligand shows important peaks at 1615(vs), 1640(vs) and 1125(m) cms^{-1}, respectively. These may be attributed to γ (HC=N) and γ (C-N) vibrations, these have been found at 1625(s), 1645(s) and 1140(s) cms^{-1}, respectively in the spectra of the complex, It appears that coordination has occurred through two nitrogen atoms of the ligand. A sharp peak in the free ligand at 1480 cm^{-1} appears unchanged in the spectra of the complex, which is due to ring vibrations. A band appears at 735(s) cm^{-1} in the spectra of the complex. It may be due to the co-ordinated water molecules, It appears, therefore, that the complex has octahedral geometry around the central metal ion, in which the Schiff base ligand molecules are acting as a bidentate ligand and two sites occupied by water molecules.

Proposed structure of the complex is-

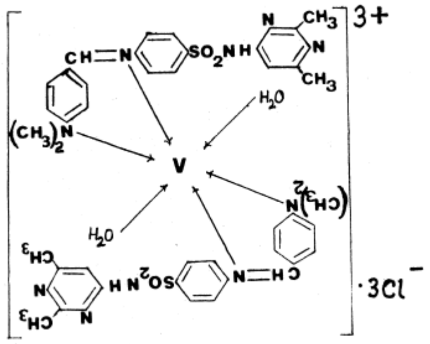


N,N'-Di methyl-4-amino benzaldehyde Sulphisomedine Vanadium (III) Chloride

On the basis of elemental analysis, the composition of red-brown coloured complex comes to be $[(C_{21}H_{23}N_5O_2S)_2.\ 2H_2O\ VC1_3]$. The melting point of the schiff base ligand is 150°C and that of the complex is 227°C. It appears that a new complex compound has been formed. The molar conductance of the complex in different solvents viz., methanol, DMF and DMSO in 0.001 molar concentration were found to be 351.6, 368.6 and 339.4 Ohm^{-1} cm^2 mol^{-1}, respectively. These values suggest 1:3 electrolytic nature for the complex. The IR spectra of the ligand exhibits some important absorption peaks at 1600(s), 1620(s) and 1135(m) cms^{-1}, these may be ascribed to γ (CH=N) and γ(C-N) vibrations, respectively. These have been shifted to 1605(vs), 1625(vs) and 1145(s) cms^{-1} in the spectrum of the complex, respectively which indicate that the co-ordination has occurred through the azomethine nitrogen and nitrogen atom of the substituted amino group.

In this way, the six co-ordination sites in the complex are occupied by two water molecules and four by two bidentate schiff base ligand molecules. A sharp peak at $750(s)^{-1}$ cm in the spectra of the complex indicate the presence of co-ordinated water molecules, In this way, complex is six co-ordinated and must have octahedral geometry around the vanadium (III) ion. The value of magnetic moment for the complex has been found to be 2.64 B.M., which is lower than expected value for two unpaired electrons.

Proposed structure of the complex is-



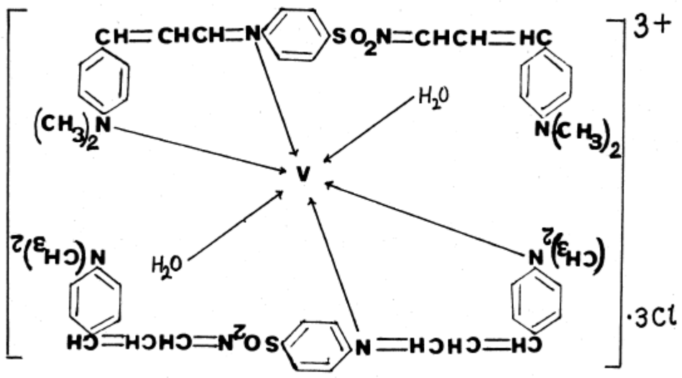
bis(N, N'-Di methyl-4-amino cinnamaldehyde) Sulphonamide Vanadium (III) Chloride

The elemental analysis suggest that vanadium tri chloride reacts with bis(N,N'-Di methyl-4-amino cinnamaldehyde) Sulphonamide in the molar ratio of 1:2. The complex so obtained is pink coloured with a composition $[(C_{28}H_{30}N_4O_2S)_2.2H_2O\ VCl_3]$. The melting point of the schiff base ligand is 230°C, while that of the complex compound is 298°C. It indicates that a new complex compound has been formed.

The molar conductance of the complex in three solvents viz., methanol, DMF and DMSO at 0.001 molar concentration exhibit its 1:3 electrolytic nature. These values are 358.1, 293.3 and 307.6 $Ohm^{-2}\ cm^{-2}\ mol^{-1}$ at room temperature, respectively.

The IR spectra of the schiff base ligand shows a number of absorption bands at 1610(6), 1625(8) and 1130(8) cms^{-1} may be attributed to γ CH-N and γ C-N vibrations, respectively. These have found in the spectra of the complex at 1620(vs), 1665(vs) and 1150(m) cms^{-1}. These peaks have been positively shifted after complexation. Similar observations have also been reported by Lehtinen and Halmekoski (151) in this field. Therefore, co-ordination has taken place through azomethine nitrogen as well as terminal nitrogen atom of substituted amino group. It suggests the schiff base is acting as a bidentate ligand. A peak in the schiff base ligand at 1495(s) cm^{-1} appears unchanged in the spectra of the complex. It is probably due to ring vibrations.

A new sharp band in the spectra of the complex appears at 730(s) cm-7. It may be due to co-ordinated water molecules. Similar behaviour has been reported by Bangres etal. (180). It, therefore, appears that the complex has octanedral geometry in which the six co-ordinated sites in the complex are occupied by two ligand molecules and two water molecules. The magnetic moment of the complex at room temperature was found to be 2.69 B.M., which is lower than expected value for d^2 system. Proposed structure of the complex is-

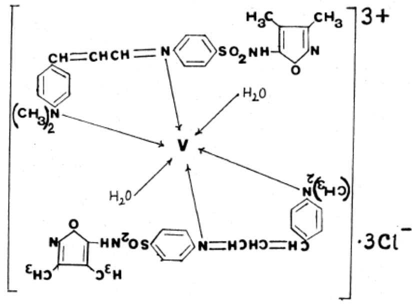


N, N'-Dimethyl-4-amino cinnamaldehyde Sulphafurazole Vanadium (III) Chloride

The schiff base ligand N,N'-dimethyl-4-amino cinnamaldehyde sulphafurazole interacts with vanadium (III) ion in 1:2 stoichiometric ratio as evidenced by elemental analysis. The formula of the complex is $[(C_{22}H_{24}N_4 0_3 S)_2.2H_20\ VCl_3]$. The melting point of the schiff base ligand is 145°C, and that of the deep green coloured complex was found to be 193°C. This indicates that a new complex compound has been formed.

The molar conductance of the complex was observed in the three solvents viz., methanol, DMF and DMSO at 0.001 molar concentration indicates its 1:3 electrolytic nature. The magnetic moment of the complex have been found 2.79 B.M. It indicates that the complex contains vanadium (III) ion, since the value corresponds to the presence of two unpaired electrons. The IR spectra of the schiff base ligand exhibit some absorption bands at 1605(s), 1625(s) and 1160(m) cms^{-1}, respectively. These may be attributed to γ CNN and γ C-N vibrations. These have found at 1620(vs), 1645(vs) and 1165(s) cms^{-1} in the spectra of the complex. These shifts suggest that the schiff base ligand is acting as bidentate because co-ordination has occurred through the nitrogen of azomethine and substituted amino group.

A sharp peak in the spectra of the schiff base ligand at 1490 cm^{-1} appears unchanged in the spectra of the complex, it may be due to ring vibrations. A sharp band in the spectra of the complex appears at 725(s) cm^{-1} , which may be due to coordinated water molecules. Thus, it appears, that the complex has octahedral geometry around the vanadium (III) ion in which the six coordinated sites are occupied by two bidentate ligand molecules, and two by water molecules. Proposed structure of the complex is-

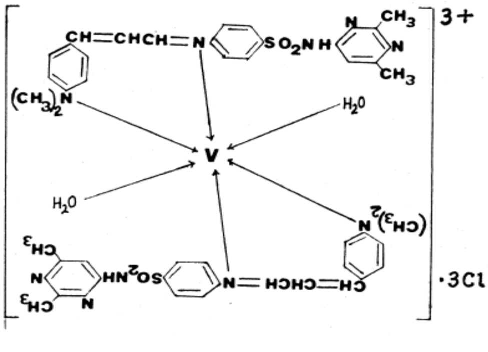


N, N'-Dimethyl-4-amino cimanaldehyde Sulphisomedine Vanadium (III) chloride

The analytical data shows that it has 1:2 metal-ligand ratio. It is an orange coloured crystalline solid. The elemental analysis for carbon, hydrogen, nitrogen, chlorine and metal helped in elucidating the composition of complex as [(C_{23} $H_{24}N_5$ 0_2 $S)_2$.2H_20 V$C1_3$). The melting point of the schiff base ligand is 110°C. However, melting point of the complex was observed as 203°C. It indicates that a new complex compound has been formed.

The molar conductance of the complex at room temperature in different solvents viz., methanol, DMF and DMSO at 0.001 molar concentration were as 325,6, 311.0 and 310.0 Ohm^{-1} cm^{2} mol^{-1}, respectively. This indicates 1:3 electrolytic nature for complex. The magnetic moment of the complex at room temperature has been found to be 2.71 B.M. It indicates that the vanadium (III) ion remains as such, since the value corresponds to the presence of two unpaired electrons. The IR spectra of the schiff base ligand show a number of absorption bands. Few significant peaks observed at 1605(vs), 1630{vs) and 1130(s) cms^{-1}, may be assigned to γ H-C=N and γ C-N vibration, respectively. These have been shifted to 1620(s), 1650(s) and 1150(m) cms^{-1}, respectively in the spectra of the complex (179). It appears that nitrogen atom of the azomethine group and substituted amino group are taking part in co-ordination.

A peak in the free ligand at 1500(s) cm^{-1} remains unaltered in the spectra of the complex. It is due to ring vibrations. A new sharp peak in the spectra of the complex appears at 740(s) cm^{-1}, it may be due to involvement of water molecules in co-ordination. Therefore, schiff base molecule is acting as a bidentate ligand. In this way, the complex have octahedral geometry in which the six co-ordination sites in the complex are occupied by two bidentate ligand and two by water molecules. Proposed structure of the complex is-



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