

A Review Analysis of Tungsten Element

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Abstract

The chemistry of tungsten is varied and complex not only because it covers nine oxidation states (-2 to +6), but also because of its ability to form complexes with different coordination numbers and geometries, and because of its tendency to form clusters and polynuclear complexes with a variety of metal atom.

Keyword: tungsten, complex compounds, Schiff base, co-ordinate compounds.

I. Introduction

The chemistry of this element has been studied since the characterization of tungstic acid in 1781 (1), and the oxychlorides, the hexachlorides and the hexabromide in 1857. Until the 1930 most of the development centered around the higher oxidation states of the element. The successful synthesis of cyclopentadienyl compound has led to the development of its organometallic chemistry. This was followed in the late 1960s and the 1970s by the synthesis and development of the chemistry of complexes containing metal-metal bonds (2).

Tungsten was discovered in 1781 in a mineral known as scheelite (1), whose principle constituent is CaWO_4 . Tungsten steel was invented in 1855 (3) and the first alloy containing tungsten were manufactured in 1868. These 'high speed steel' have been used ever since as cutting tools because of their hardness even at high temperature. Because of its high melting point, it has been used as a filament for incandescent lamp (4) since 1904, and for a long time this was its principal application. More recently, there has been increased interest in alloys containing tungsten, as material for high temperature application.

The element shows quite a varied chemistry in (VI) oxidation state, because the hexahalides are reasonably stable and give rise to a variety of substitution products of the type $[\text{WX}_{6-n}^{\text{L}}]$ [n=1-6].

The three hexahalides WF_6 , WCl_6 , and WBr_6 are known and synthetic routes to their preparation are summarized. WF_6 is a colourless gas while WCl_6 & WBr_6 are blue black moisture sensitive solids. Under well-defined conditions, the octahedral hexahalides undergo substitution to give products of the type $[\text{WX}_{6-n}^{\text{L}}]$ (n=1-6). Mix fluoro chloro compounds have reported to result from reaction of WCl_6 with F_2 or from WF_6 with Me_3SiCl (5).

Halide substitution by ligand containing Nitrogen, oxygen and sulphur donor atoms are also known. The reactions of WCl_6 with NCS^- leads to $[\text{W}(\text{NCS})_6]$ (6), WF_6 reacts with $\text{Me}_3\text{SiNEt}_3$, to give $[\text{WF}_5\text{-NEt}_3]$ and $\text{cis}[\text{WF}_4(\text{NET})_2]$ (7). An interesting six co-ordinate complex results from the reaction of WCl_6 with LiNMe_2 , (8). Crystal structure analysis (9) of $[\text{W}(\text{NMe}_2)_6]$ shows that the complex is octahedral with an average W-N distance of 2.023 Å. It reacts with ROH (R=Me, Et, Pr, Pr) (10) to give the known W(OR), compounds. With MeOH, under certain conditions, $\text{fac-}[\text{W}(\text{NMe}_2)_3(\text{Ome})_3]$ is obtained (10).

Several other W^{VI} complexes with co-ordination number greater than six have been reported. $[\text{W}(\text{Me})_6]$ reacts with tertiary phosphines to give the seven co-ordinate adducts $[\text{W}(\text{Me})_6\text{L}]$ (L= PMePh_2 , PMe_2PH , PEtPh_2 , PMe_3) (11 & 12). The best characterized of these is the PMe , adduct, which was shown by ^1H and ^{13}C NMR to be fluxional at room temperature, although a rigid structure such as a capped bipyramid exists at low temperature. With excess MeLi $[\text{W}(\text{Me})_6]$ gives the bright yellow eight co-ordinate compound $\text{Li}_2[\text{W}(\text{Me})_8]$ which is reasonably stable as the dioxane solvate (13).

$[\text{WMeCl}_5]$ was reported to react with octamethylphosphoramide and diphos to give the adducts $[\text{WMeCl}_5\text{L}]$ which are believed to be eight co-ordinate

Several Nitrogen complexes of W^{VI} are known. WCl_6 reacts with CIN_3 (14) to give $(\text{WNCl}_3)_4$ whose structure is believed to be tetrameric similar to that of its molybdenum analogue (15) $(\text{WNCI}_3)_4$, can also be prepared from WCl_3 , and IN_3 (16). Impure $(\text{WNB}_3)_4$ has been prepared from WBr_6 , and IN_3 , (16). The preparation of $(\text{WNCI}_4)_4$ has been reported and $(\text{W}_2\text{NCI})^{-2}$ was isolated from this preparation (11). The structure of this dinuclear complex consists of W^{VI} linked by a linear asymmetric nitride bridge,

With py, the adducts $(\text{WNCI}_3)_3\text{py}$ of unknown structure is obtained (12). Other characterized complexes derived from $[\text{WNCI}_3]$ are $(\text{WNCI}_3)_3$, PPh_3 , $[\text{WNCI}_5]$ and WNCI_3 (bipy) (13). The reaction of $[\text{WNCI}_3]$ with POCl_3 , gives the tetranuclear compound $[\text{WNCI}_3, (\text{OPCl}_3)]_4$ * This structure consists planar

square W_4N_4 eight membered ring with alternating W-N bond lengths and the presence of the nitride ligand is easily detected in these complexes by a strong IR absorption band around 1050 cm^{-1} assigned to $\nu(W-N_i)$ (13).

The co-ordinatively unsaturated $\{WOX_4\}$ complexes reacts with ligands such as alkyl cyanides, THF or Py to give the six co-ordinate $[WOX_4L]$ complexes (14 & 15). $WOCl_4$ reacts with bidentate Schiff bases to give complexes of the type $[Woci, (\text{Schiff base})]$ (16). These complexes show one $(W-O_i)$ at around 970 cm^{-1} , with tridentate schiff bases, $[WOCl_2(\text{Schiff base})]$ is obtained complexes of the type $[WOF_3 L^-]$ (L^- =bidentate hydroxy acid) have also been reported (17).

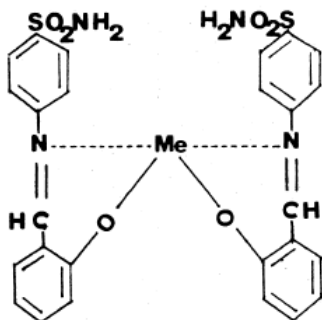
The structure of the azoxybenzene adduct of $WOCl_4$, has been reported (18). The azoxybenzene ligand is co-ordinated through the oxygen atom trans to the oxoligand with a bond length of 2.276 \AA . The W-O distance is 1.669 \AA .

Schiff (19) reported the formation of a new type of compounds prepared by the condensation of primary amine with carbonyl compound and since then the condensation products are referred to as Schiff bases. Primary amine generally undergo condensation reaction with aldehyde resulting in the formation of the schiff bases. Schiff bases contain a carbon-nitrogen linkage known as azomethine linkage. The Schiff bases derived (20 & 21) from aromatic aldehydes and amines have attracted a great importance in the preparation of pharmaceutical agent (22 & 29).

S.J. Gruber et al. (30-32) emphasized the metal complexes of tetradentate schiff bases, such as salicyldimines may act as bidentate chelating agents co-ordinating through this: oxygen atom to form a trinuclear metal complexes.

Dwyer et al. (33) prepared some hexadentate ligands by using salicylaldehyde, pyridine-2-carboxaldehyde and 2-amino methyl, 3-diaminopropane. The interacting of these ligands with Iron (II) and cobalt (II) salt gave the stable adducts. In case of iron the ligands were found to have as hexadentate but in cobalt (II) it appeared to co-ordinate as quinquidentate type.

Macarorici and C. Macarorici (34) discovered the method of preparation of Cu (II) and Co (II) chelates of schiff bases formed from some sulphonamides and salicylaldehyde or its derivatives. The general structure given below, has been suggested for the chelates.



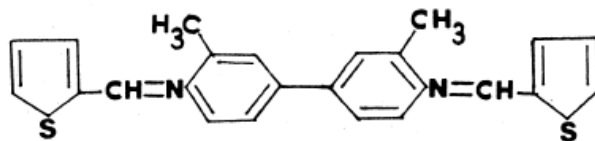
Patel & Manavalan (35) prepared the co-ordinated complexes of Cu(II), Co (II), Ni (II), Zn(II), Cr(III), Fe(III), oxovanadium (IV) and dioxouronium (VI) with salicylic acid thiourea-trioxane copolymer. The analytical data agreed with 1:1 metal ligands stoichiometry. Elemental analysis, magnetic properties, spectral properties, T.G.A. and electrical conductivity for the polymer and its chelates were studied, and structure were assigned to the co-ordinate complexes. All the chelates were amorphous powder, insoluble in common organic solvents and showed slight solubility in DMF.

Lehtinen & Halmekoski (36) prepared Cu (II) and Co (II) chelates of the schiff bases obtained from sulphonamide and salicylaldehyde and its HO- and Br- derivatives and to analyse and investigate the thermogravimetric properties of these chelates. Patil (137) et al. studied the five co-ordinated VOL ($H_2L = 5-R-2HOC_6H_3CH: NNH_2$) C:S, R-H, CH_3 , OMe, Cl) and six co-ordinated UO,L prepared in EtOH and characterized by IR electronic, NMR, ESR, spectra. The ligand co-ordinated through azomethine, N-atom and deprotonated hydroxy O-atom. The $\nu(M-N)$ and $\nu(M-O)$ vibrations were assigned. The magnetic moment of VOL are $1.74-1.94\text{ \mu B.M.}$

Jain (38-40) *et al.* have studied the chelate formation and the stability of schiff bases derived from salicylaldehyde and sulphonamides by the potentiometric method in an acetone-water or dioxane water solution.

Mohd. Athar and Naseer Ahmed (41) prepared and characterized complexes of bis (thiophene-2-carboxaldehyde), O^- -tolidine, (where O^- -tolidine = 4, 4-diamino-3, 3, dimethyl biphenyl with various transition metal ions; viz.; Mn(II), Fe(II), Co(II), Ni(II) Cu(II), Ru(II), Pd(II), Ir(IV), Pt(IV) and Au(III)). The complexes were characterized on the basis of analytical, conductance, I.R. spectra electronic spectra and magnetic moment data. IR spectra of the complexes show that the ligand act as a tetradentate molecule. Molar conductance in DMF indicates that Rh(III), Pr (IV) complexes are nonelectrolyte where Co(II), Cu (II), Ru (III) and Au (II)

complexes are 1:1 electrolyte and 1:2 electrolyte nature is shown by the complexes of Mn (II), Fe (III), Ni (II) and Pd (II). Only Pt (IV) complexes exhibits 1:4 electrolyte nature. They also studied the E.S.R. spectrum of Cu (II) complex and explained the compressed rhombic symmetry with a distorted trigonal bipyramidal geometry.



Vasudha Atre (42) *et al.* studied the complexes of Cu (II), Ni(II), Cd (II), Fe (II), Mg (II) and Zn (II) with schiff bases derived from 2-hydrazinobenzoxazole and salicylaldehyde. Complexes were prepared by refluxing the methanolic solution of metal chlorides (0.001M) and the ligand (0.002M) for 3 hours. The Cu (II) complexes separated out immediately as a green crystalline compound. The chelates of other metal ions separated in raising the pH to 8 by addition of ammonia solution (1:1). The separated products were filtered washed with hot methanol followed by pet. ether (60-80°C) and dried in vacuo. Elementals, magnetic susceptibility measurements and thermogravimetric analysis were characterized by the methods Reddy & Tyagi *et al.* IR spectra was also recorded. Electronic spectra and ESR spectra was recorded in nujol-mull at room temperature on UVvisible spectrophotometer DMR-21 and EPR-4, spectrometer, respectively. The analytical results indicate 1:1 (M:L) stoichiometry for all the complexes except the Cu(II) complex, where 1:2 stoichiometry is found. The complexes are soluble in DMF, DMSO and dioxane. The molar conductance values of 1×10^{-3} M solution of the complexes in DMF (2-20 mho $\text{cm}^2 \text{mol}^{-1}$) show then to be nonelectrolyte.

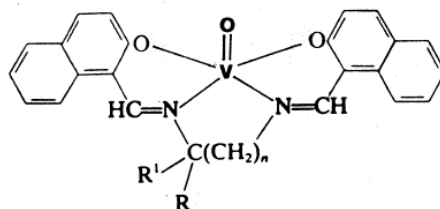
Jezowska (43) *et al.* studied the IR spectrum of Nsalicydene-*o*-hydroxymethylaniline and its complexes of Fe (III), Co (II), Ni(II), Cu(II) and Zn (II). The spectrum of $[\text{FeCl}]_2$, shows absorption at 1607 cm^{-1} , characteristic of the coordinated C=N-group. The band at 1540 cm^{-1} is connected with the phenolic C-O stretching vibrations and appears in the region characteristic for a co-ordinated phenolic group. Some of the other bands may be tentatively assigned as follows, $3050, 760 \text{ cm}^{-1}$ -aromatic C-H, $2850, 2930 \text{ cm}^{-1}$ -CH₂, stretching, 1490 cm^{-1} -CH₂ scissors, $1580, 1467 \text{ cm}^{-1}$. C=C aromatic, 1019 cm^{-1} alkoxy C-O stretching. The IR spectrum of $[\text{CoL}(\text{H}_2\text{O})_2]_2$ is similar to that of $[\text{FeLCl}]$ in the region $700\text{-}1700 \text{ cm}^{-1}$. Again the position of the phenolic C-O stretching band i.e. 1553 cm^{-1} indicates the lack of phenoxy bridges. The weak and broad band at Ca. 3260 cm^{-1} may be attributed to γ -OH vibration of a co-ordinating water molecule. The broadening of this band may be caused by strong intermolecular H-bonds.

IR spectrum of $[\text{NiL}(\text{H}_2\text{O})_2]_2$ is almost identical with that of $[\text{CoL}(\text{H}_2\text{O})_2]_2$ even in the 'finger print' region so the same assignment were made $[\text{CuL}]_n$ show no band and is very similar to that of Fe and Co complexes in the region $700\text{-}1800 \text{ cm}^{-1}$ $[\text{Zn-L}]$ exhibits broad, weak γ -OH absorption at Ca. 3340 cm^{-1} and the other band positions are almost identical with that of cobalt or nickel complexes except for small changes in the 'finger print' region.

Syamal (44) has reported some new antiferromagnetic copper (II) complexes with same dibasic tridentate ONS donor schiff bases. The schiff bases were prepared from salicylaldehyde, 5-chlorosalicylaldehyde, 5-Bromo Salicylaldehyde, 4-methoxy salicylaldehyde, 5-methoxy Salicylaldehyde and 3-amino thiophenol dibasis ligands. The complexes were characterized by elemental analysis, IR and electronic spectra as well as magnetic susceptibility measurements. These complexes are insoluble in common solvents and decompose at 200°C with melting. The complexes possess subnormal magnetic moment ($\mu_{\text{eff}} = 1.3\text{-}1.5 \text{ B.M.}$ at room temperature) and are antiferromagnetic exchange with a S=O ground state.

Syamal and Gupta (45) show a new platinum (II) complexes of schiff bases derived from aniline and salicylaldehyde, 5-chloro salicylaldehyde, 5-Bromosalicylaldehyde, 5-Nitrosalicylaldehyde, 3-ethoxysalicylaldehyde and 2-hydroxy-1-naphthaldehyde have been reported. The complexes were found by an addition of an aqueous solution of potassium tetrachloroplatinate (II) in an aqueous solution (2ml) of KOH. The resultant solution was added to an ethanolic solution of the appropriate Schiffbases. The mixture was refluxed over a water bath for 2 hr. The solid compound was obtained after partial evaporation of the solvent under a fan. The compound was recrystallized from 1:1 water ethanol mixture followed by petroleum ether and dried in vacuo at room temperature. The metal contents in the complexes was determined gravimetrically by igniting the complexes and weighing as Pt. carbon, hydrogen, and nitrogen. Analysis were done microanalytically, the IR spectra were recorded in nujol-mull using a Beckman IR-20 IR spectrophotometer calibrated with polystyrene. The analytical data shows that the complexes are of the type PtL_2 (where LH = schiff base), having non-electrolytic nature. The complexes are diamagnetic as expected for the $5d^8$ platinum (II) ion,

Patel and Kalawole (46) have studied the magnetic and spectral properties of oxovanadium (IV) complexes of quadridentate naphthaldimine ligand. They found that the magnetic moments of complexes were in the range $1.5\text{-}1.77 \mu\text{B.M.}$, at room temperature.



(where $n = 2$, $R = \text{H, Me}$, $R^1 = \text{Me}$) and $n=2-8$ ($R=R' = \text{H}$)

Kuge and Yamada (47) reported the oxovanadium (IV) complexes of tridentate dibasic ONO donor schiff base derived from salicylaldehyde derivatives and alkonalamine were prepared and fully characterized by elemental analysis, IR and electronic spectra magnetic susceptibility measurements and thermal analysis. The structures for these complexes are multinuclear in the solid state and binuclear in CH_2 , Cl CH_2 , Cl . In pyridine solution their multinuclear structure is broken and uninuclear pyridine adducts are formed.

Sharma and Islam (48) separated the octahedral $[\text{VOL}_2\text{L}^1_3]$, $(\text{VOL}_2\text{L}^2(\text{H}_2\text{O}))$, $[\text{VOL}(\text{OH})(\text{H}_2\text{O})_2]$, $(\text{TiL}_3\text{L}_3^1)$, $(\text{TiL}_3\text{L}^2(\text{H}_2\text{O}))$ and $[\text{TiL}_2(\text{OX})(\text{H}_2\text{O})_2]$ ($\text{HL} =$ phthalimide ; succinimide ; $\text{L} =$ quinoline, isoquinoline; picoline or pyridine, L4-2, 2-bi pyridine, 1, 10-phenanthroline or 2-aminopyridine and hydroquiline) complexes and characterized by elemental analysis, magnetic moment measurements and IR and electronic spectroscopy.

Mishra and (Km.) Purohit (49) have prepared $\text{M}(\text{Vol}_2, \text{x})$ $\text{HL} =$ acetylaceton, oxime, pyridine carboxylic acid, $[\text{M}=\text{K}, \text{X}=\text{SCN}^-, \text{M}=\text{Na})$ and characterized by IR \AA UV spectra and magnetic moments. L co-ordination as tridentate ligands, so that v is in distorted octahedral environment.

Mohamed (50) *etal.* reported cobalt (II), Nickel (II), Thorium (II) and uranium (VI) complexes of some heterocyclic schiff base derived from hydroxy aromatic aldehyde and 2-amino pyridine. The complexes were characterized by chemical analysis, IR, UV spectra and conductometric titration studied.

Lehtinen and Halmekoski (51).reported three distinctly separated absorption peaks in the ultra violet range of the absorption spectrum of most of the synthesized schiff bases. The synthesized schiff bases of 4-OH-salicylaldehyde and sulphanilamide and 5-Bromosalicylaldehyde and sulphafurazole have only two peaks. These three maxima were found at 308-355 nm, 269-280 nm and 230-242 nm and the IR spectrum of the schiff base containing substituted salicylaldehyde and sulphanilamide shows an absorption band in $1610-1630 \text{ cm}^{-1}$ range, while those derived from salicylaldehyde sulphafurazole or sulphamethoxy pyridazine and sulphamethiazole exhibited two bands at slightly higher ($1620-1650 \text{ cm}^{-1}$, wave number region.

Agarwal and Gyanendra (52) synthesized and characterized the complexes $\text{VO}(\text{benzoquo})$, X , ($\text{benzoquo} - 5,6 - \text{benzoquinoline N - oxide}$, $\text{X} = \text{Cl, Br, I, NO}_3, 0.5 \text{ C}_2\text{O}_4$ and $[\text{VO}(\text{benzoquo})_4](\text{ClO}_4)_2$, by chemical analysis, magnetic susceptibility, IR and electronic spectra. The complexes are 5-co-ordinated have tetragonal pyramidal structure. Thermal properties of the complexes have also reported.

Syama and Kale (53) synthesized copper (II) complexes of tridentate dibasic schiff bases. They obtained schiff bases, using salicylaldehyde 5-Bromo salicylaldehyde, 5-chlorosalicylaldehyde, 3-methoxy-salicylaldehyde, 3,5-dichlorosalicylaldehyde and o^- -aminobenzyl alcohol. The complexes were characterized on the basis of elemental analysis, IR & electronic spectra and magnetic susceptibility measurements. They described that schiff bases behaved as tridentate dibasic ONO donor type, forming complexes with 1:1 (metal · ligand). stoichiometry. The complexes exhibited subnormal magnetic moment $\mu_{\text{eff}} = 0.98-1.48 \text{ B.M.}$ at room temperature).

Dashora (54) *etal.* have reported organosilicon and organo lead complexes of schiff bases derived from sulphadiazole. The electronic spectra were recorded on a pye-unicam SP 8-100 spectrophotometer in the range 20-60 nm. IR spectra were scanned on a Perkin-Elmer 577 grating spectrophotometer in nujol-mull in the range $4000-400 \text{ cm}^{-1}$.

Syama and Gupta (55) showed the IR spectrum of the schiff bases derived from aniline and salicylaldehyde or substituted salicylaldehyde and its complexes with platinum (II) complexes of ON donor. The schiff bases exhibit an IR band around 2800 cm^{-1} , which is assigned to the intramolecularly hydrogen bonded $\gamma(\text{OH})$. The free schiff bases exhibit in the IR spectrum a strong band at $1615-1625 \text{ cm}^{-1}$ which is assigned to the $\gamma(\text{C}=\text{N})$ mode. This band shifts to lower energy side by $5-30 \text{ cm}^{-1}$ in the complexes indicating co-ordination of nitrogen to the metal ion. The $\gamma(\text{C}-\text{O})$ (phenolic) mode is observed in the IR spectrum of free ligand in the region $1515-1535 \text{ cm}^{-1}$. This relative higher energy value is due to the partial double bond character of the C-O band because of the neighbouring benzene ring. Thus the $\gamma(\text{C}-\text{O})$ (phenolic) mode should occur at a lower energy than the $1 \gamma(\text{C}-\text{O})$ (phenolic) mode. On complexation the $1(\text{C}-\text{O})$ (phenolic) mode shifts to higher energy side by $5-10 \text{ cm}^{-1}$ indicating co-ordinating of phenolic oxygen of the schiff bases.

Gupta and Jha (56) isolated antimony trichloride complexes of sulphanilamide, sulphathiazole, sulphapyridine, sulphamerazine and sulphamethiazole. Complexes of antimony trichloride with sulphonamides

were prepared by the interaction of methanolic solution of antimony trichloride and sulphonamides in 1:1 and 2:1 molar ratios keeping antimony trichloride in slight excess. Infrared spectra were recorded in KBr on a Unicam SP-1200 spectrophotometer in the range 4000-400 cm^{-1} .

Although we made to prepare both 1:1 and 2:1 complexes of antimony trichloride with all the sulphadiazine drugs by taking the reactants in appropriate molar ratio, but all the desired complexes could not be obtained. Only sulphamethazine yielded both 1:1 and 2:1 complexes, while sulphamerazine formed 2:1 complexes, rest of the drugs formed 1:1 complexes only. All the complexes are light yellow and melt much below the melting points of the corresponding sulphonamides except for the sulphanilamide complexes which melt above the melting point of the drug.

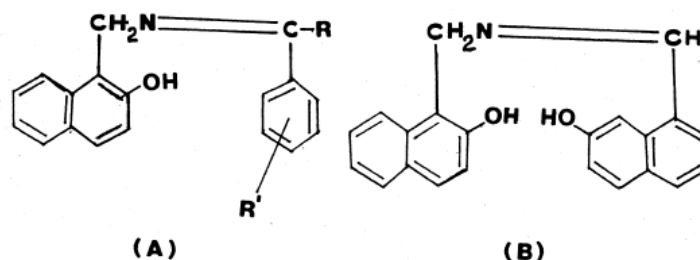
Nate (57) *et al.* have reported the tridentate dibasic Schiff bases salicylideneanthranilic acid (H_2SB) reacts with VOCl_2 in the presence of NaOAc and imidazole or its derivatives (L) to form $(\text{VO}(\text{SB})(\text{L}))_2$. These green and yellow compounds have a magnetic moment 1.4 B.M. at room temperature and are non-electrolytes in MeOH. The compounds were characterized on the basis of IR spectra as well as EPR spectroscopy. The IR spectra shows a strong band due to (1:0) at 880 cm^{-1} in addition to the band of H_2SB and imidazole. $\text{VO}(\text{SB})(\text{IM})_2$ (Im = Imidazole) shows a single unresolved EPR signal at $g=1.9715$ where compound containing other imidazole derivatives shows both a broadening and shifting of the signal. Thermogravimetric measurements indicate the stability of the complexes and their stepwise thermal decomposition.

Hossain and Dutt (58) have studied chelate exchange reaction between bis(acetylacetonato)oxovanadium (IV) and salicylidenebenzoyl hydrazone, Schiff bases. They found that these reactions depending upon the relative amounts of reactants, chelate exchange between $\text{VO}(\text{acac})_2$ (acac = Acetylacetonato) and salicylidene (benzoyl) hydrazone type Schiff bases (H_2L) provides VOL and VL_2 . VOL were found to have subnormal magnetic moment and possess metal-metal interaction dimeric forms. VL_2 have normal magnetic moment of 1.7 $\mu\text{B.M.}$ These complexes were characterized by elemental analysis, IR & electronic spectra and magnetic moments.

Varshney and Tandon (59) synthesized Tin (II) and Ti (IV) complexes of macrocyclic Schiff base. The complexes were analysed and IR spectra were recorded on a Perkin-Elmer 577 IR spectrophotometer in the region 4000-200 cm^{-1} using KBr optics. IR spectra showed the strong band around 1620 cm^{-1} assigned to $\text{C}=\text{N}$ is shifted to a higher wave number in the spectra of the adducts, and this indicates co-ordination of the ligand through the nitrogen atom of the azomethine group. The new bands around 430 and 600 cm^{-1} in the complexes could be assigned to $\gamma(\text{N}+\text{Sn})$ and $(\text{C}-\text{Sn})$, respectively.

Lehtinen (60) reported the chelate formation of Cu (II), Co (II) and Ni (II) with the Schiff bases formed from 5-bromo salicylaldehyde and the medicinal sulphonamides sulphamethoxypyridazine, sulphamethizole and sulphafurazole in non-aqueous solvent mixture which showed the difference in the stability by the chelates of 5-bromo-SA-sulphamethoxypyridazine was small. The difference was more significant in the case of chelates of 5-Br-SA-sulphamethizole showing about tenfold stability for the Ni(II) chelate as compared with that of the Co (II) chelate.

Havinala and Pujar (61) reported dimeric square pyramidal oxovanadium (IV) complexes of bifunctional tridentate Schiff bases. The Schiff bases were of type A & B



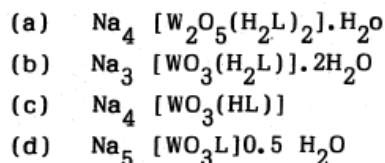
I; ($\text{R}=\text{H}_2$, $\text{R}'=\text{H}_2$, 5MeH, 3MeO, 5C1; $\text{R}'=\text{Me}$, $\text{R}=\text{H}$)

Reaction of $\text{I}(\text{R}=\text{R}'=\text{H})$ with VOSO_4 gave the corresponding complexes of empirical formula $(\text{C}_{18}\text{H}_{13}\text{NO}_2)_2\text{VO}$. The complexes exhibited subnormal magnetic moments, (i.e. 0.91-1.13 $\mu\text{B.M.}$) at room temperature due to strong antiferromagnetic exchange.

Oxovanadium (IV) complexes with ONS donor tridentate Schiff bases derived from thiosemicarbazide and β -diketones were studied by Syamal (162) *et al.* These complexes exhibited subnormal magnetic moments of 1.44-1.58 $\mu\text{B.M.}$, indicating the presence of antiferromagnetic exchange.

Hills (63) *et al.* have reported that the oxidation of $[\text{VO}(\text{Salen})][\text{H}_2\text{salen}=\text{N}, \text{N}-\text{ethylene bis(salicylideneimine)}]$ with I_2 produces a mixed V(IV)-V(V) species $[(\text{Salen})\text{VOVO}(\text{Salin})][\text{I}]$, (I) as detected by X-ray crystal structure analysis.

Asatryan (64) et al. have synthesized the complexes of W(VI) with glycinebismethylphosphate acid (H₂L) and characterized by IR, ESR, element analysis and thermogravimetric analysis, the complexes have the following compounds



Karwecka (165) has reported reaction of VCl₃ and VOCl₃ with phenols (L- pyrocatechol, phrogallol) and investigated spectrophotometrically and conductometrically in EtOH solution. The formation of bright-colour, polynuclear V(III) [V₂L₂Cl₂]⁺ and mononuclear V(IV) (VOL(EtOH)₂Cl)⁺ complexes have been discussed.

Hughes (66) *et al.* emphasized the tungsten (IV) complex with cyclooctasulfua ligand prepared by W(CO)₆ with SnCl₂ under CH₂Cl₂ irradiation give the little dark red complexes WC₁₄S₈. shown by X-ray crystallography to have a monomeric, square pyramidal WC₁₄S unit with apical S and with an S₈ molecule occupying a position below the CCl₄ plane, trans to the terminal sulfide ligand.

Hossain (67) synthesized BZNHN:CMech₂CMe : NCH₂CH₂N : CMeCH₂Ac(H₂L), ML.H₂O (M= Ni, Cu) and (Co(H₂L)Cl) H₂O complexes and characterized by magnetic susceptibility, Magnetic moments indicates spin-spin interconverting mixture of a square plane dimagnetic Ni complex (ONNN Co-ordination).

Monzer (68) has reported cyclopentadienyl complex of titanium (III) and Vanadium (III) by treatment of MCl₃ (M=Ti, V) with Tl (C₅H₅) C₅H₅ cyclopentadienide) is tetra hydrofuran afforded MC₁ (- c Hz), in 93. 8-97.5% yeild, complexes were characterized by chemical analysis Viz., UV-Visible, IR, electronic spectra, magnetic moment and thermogravimetric analysis.

Buglyo and Kiss (69) have studies the formation of a tris complexes in the Vanadium (IV) tiron system. The formation of a tris complexes, VA, was detected by pH metrically in the oxovanadium (IV) tiron (1,2, dihydroxybenzene-3, 5-disulfonate) system and its draft stability constant was detected. The slow formation of the tris complex in both acidic and basis solution was studied in detail via a combined pH-spectrophotometric method. Spectrophotometric titration at 25.04.0.1° and ionic strength 0.2 mol/dm³ (KCl) yielded a log K value of 2.01±0.03 for the formation process VOA₂ +H₂A= VA₃+H₂O

Cherkasova (70) *et al.* have synthesized Vandium (IV) complexes with dimethyl sulfoxide and DMF. (VO)₃ [Cr(SCN)₆]₂. 15L (L=DMSO, DMF) were prepared from VOCl₂.3L. 2H₂O and K₃[Cr(Scn)₆] in aqueous solution. Both were characterized by IR spectra, electrical conductivity measurements, thermal stability studies and X-ray diffraction both (L) are O-bonded.

Abu-El Wofa and Issa (71) hour reported the formation of chlorovanadium (III) and Vanadium (IV)-N₂O₂-schiff bases complexes, characterized by spectral and magnetic studies. VLCl (H₂L= bis(salicylidene) and bis (2-hydroxynaphthylmethylethylenediamine)and V₂L'C₁₄ (H₂L'-bis(2-hydroxy, 1naphthylmethylene-1,9-nonanediamine and p⁻-biphenyldiamine) were prepared.

Simpson and Pierpont (72) have studied complexes of Vanadium(III) and Vanadium (IV) containing bipyridine and tetrachloroate-chelate ligangs. The reaction between V(acac)₃ (Hacac=2,4 penta-anediene), tetrachlorocatechol (H₂Cl₄cat) and 2,2'-bipyridine (bpy) gives Vibpy) (acac) (C₁₄cat.) and CH₂Cl₄ (I) and V(bpy) (C₁₄cat)₂(II). Crysallographic characterization of (II) [tridinic, space. group P₁, Z=2, R=0.065, R_w=0.076] shows that it has a trigonal prismatic structure with a twist angle between triangular faces of 3.2° (II) appears to result from oxidation of the V(III) species fromed initially in the reaction. Crystallographic characterization of a thin plate- like crystal of (I) (monoclinic, space ground P_{21/n}, Z=4, R=0.056, R_w=0.074) shows that it is octahedral and monomeric.

Uzoukwu (73) synthesized, structure, UV-visible and IR spectral studies of 1-phenyl-3-methyl-4-acyl-5-pyrazolone complexes with V(IV). VOX₂ (HX= 1-phenyl-3-methyl-4acylpyrazolone, acyl acetyl, propionyl, butyryl, valeroyl, Caproyl, benzoyl, trifluoroacetyl, trichloroacetyl) were prepared and characterized using UV-visible and IR spectral studies. The V:O appeared at 895 cm⁻¹, and this low absorption band is attributed to a possible presence of bridging Vo groups in the complex, ²E_g -²T_{2g} transition were observed with in the (24.729.4) X 10³ cm range due to an octahedral field in the complexes

Mikulski (74) *et al.* have reported Vanadium (III) chloridexhypoxanthin and xanthine complexes. V(LH)₂ LCl₃ (LH=hypoxanthine, xanthine) were prepared and characterized by IR and electronic spectra and magnetic susceptibility measurements. These complex form linear chain with bridging L⁻.

Liu and Xu (75) studied dioxomolybdenum (IV) complexes with schiff bases derived from salicylaldehyde and O⁻-hydroxybenzylamine. MoO₂L (H,L= Salicylaldehyde-O⁻- hydroxybenzylamine) and MoO₂LQ (Q=py, DMSO) were synthesized and characterized, using elemental analysis and IR spectra.

Salam (76) *etal.* have reported dioxomolybdenum (IV) complexes with some schiff bases and characterized by IR. spectra and magnetic moments measurement. Thirteen MoO_2L (HL= schiff bases of ethylen diamine or 1,3-propanediamine with acetylacetone, benzoylacetone, dibenzoylmethane, salicylaldehyde, 5-Bromo-salicylaldehyde, 2-hydroxy-1-naphthaldehyde, 2hydroxyacetophenone, Et.acetoacetate), were prepared from cis Moo, (acac) (H acac \acute{a} acetylacetone). IR data suggested the presence of MoO_2 of the Moiety. Diamagnetic behaviour observed for the prepared complexes indicates the +6 oxidation state of molybdenum. The conductance and the electronic spectral measurement helped assign electrolytic and structural behaviours of the prepared complexes.

Rizvi and Ahmad (77) synthesise titanium (III) complexes with schiff bases, viz., bis(Vanilline) benzidene, bis(Vanilline) O⁻-dianisidine, bis(Vanilline) O⁻-phenyl enediamine, bis (Vanilline ethylene diamine, bis(vanilline) propylene diamine, bis (salicylaldehyde) O⁻ phenylene diamine and bis. (benzaldehyde) O⁻ phenylene diamine, respectively. The complexes were characterized by elemental analysis, TGA molar conductance, infra red spectra, magnetic moments.

Rizvi & Ahmad (78) reported Ti (III) complexes with schiff bases formed by combining derivatives of benzaldehyde with benzidine, di-anisidine and O⁻-phenylenediamine in 2:1 molar ratio. The complexes formed were in the stoichiometric ratio of 1:1. The molar conductance of the complexes were in between 25.2 and 70.6 $\text{ohm}^{-1}\text{cm}^2 \text{mol}^{-1}$ in DMSO which is quite compatible with the range for 1:1 electrolyte.

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