I. GENERAL CHEMISTRY OF VANADIUM

Vanadium is a ubiquitous element dispersed throughout the earth’s crust, rivers, lakes and oceans. The formation of an oxide layer stabilizes the metal against oxidation. Pure vanadium is a bright white metal, and is soft and ductile but traces of impurities makes it hard and brittle. It is solid at room temperature and melts at 1910°C. Nearly ninety minerals containing vanadium are known but, since concentrated deposits are very few, its extraction is not very economical. The most important minerals are patronite (V₂S₅), Vanidinite (Pb₅(VO₄)₃Cl) and carnotite (K(UO₂)₂VO₄.3/2 H₂O). The last one is most important because of uranium context. Vanadium was discovered by Andres manuel del Rio, a Mexican chemist in 1801. Unfortunately, a French chemist incorrectly declared that Del Rio’s new element was only impure chromium. The element was rediscovered by Nils Gabriel Sefstrom in 1830.

The chief applications of vanadium is in steel industry where it is used in the form of ferro-vanadium alloy (an alloy of iron and vanadium) for making special steels. Vanadium is used as a catalyst in the oxidation reactions of certain organic compounds. V₂O₅ is used as a catalyst in contact process for the manufacture of Sulphuric acid. Vanadium is a powerful alloying agent; a small amount adds strength, toughness and heat resistance. Alloys of vanadium, with titanium, copper and aluminium are used in industry for various purposes, in particular for standing high temperatures. Vanadium-aluminium-titanium alloys are used in high-speed airframes and jet engines. Vanadium has good corrosion resistance to alkalis, sulphuric acid, hydrochloric acid and salt water due to the formation of a surface film of oxide. At room temperature it is not affected by air, water or acids, other than HF with which it forms complexes. However, the metal dissolves in oxidizing agents such as hot concentrated H₂SO₄, HNO₃ and aqua regia. Naturally occurring vanadium is a mixture of two isotopes, \(^{50}\text{V}\) and \(^{51}\text{V}\). \(^{50}\text{V}\) is slightly radioactive, having a half-life of >3.9x \(10^{17}\) years. \(^{51}\text{V}\) has a nuclear spin 7/2 which is useful for NMR spectroscopy. A number of 24 artificial radioisotopes have been characterized, ranging in mass number from 40 to 65.
The most stable of these isotopes are $^{49}$V with a half-life of 330 days, and $^{48}$V with a half-life of 16.0 days. All of the remaining radioactive isotopes have half-lives shorter than an hour, most of which are below 10 seconds. At elevated temperatures vanadium reacts with air or oxygen to form oxides of the type $V_2O_3$, $VO_2$ and $V_2O_5$. The metal also reacts with $N_2$ and C at high temperatures forming interstitial nitrides VN and carbides VC and VC$_2$ respectively. On heating with $H_2$, the element forms non-stoichiometric hydrides. It also forms halides in different oxidation states such as VF$_5$, VCl$_4$, VBr$_3$ and VI$_3$. The maximum oxidation state for vanadium is +5. The element shows full range of oxidation states ranging from -1 to +5. The compounds of vanadium in the lower oxidation states are good reducing agents. They are also ionic in character and on account of complete electron shells, they are also coloured. The +4 oxidation state is stable and +5 is slightly oxidizing. Vanadium(IV) compounds often exist as vanadyl derivatives which contain the VO$^{2+}$ center. Lower oxidation states occur in compounds such as V(CO)$_6$, [V(CO)$_6$]$^-$ and substituted derivatives.

II. COMPLEXES OF VANADIUM IN DIFFERENT OXIDATION STATES

OXIDATION STATE (V)

Vanadium(V) has a great affinity for O-donor. Vanadium(V) oxide is obtained on burning the finely divided metal in an excess of oxygen. The usual method of preparation is by heating ammonium metavanadate (Scheme 1).

\[
2NH_4VO_3 \xrightarrow{} V_2O_5 + 2NH_3 + H_2O
\]

Scheme 1

Vanadium(V) forms many complexes and probably the best known are white, diamagnetic hexa-fluorovanadate, MVF$_6$, which are extremely sensitive to moisture. In aqueous solution of vanadium(V), various peroxo complexes can be formed by the oxidation of $H_2O_2$ depending on the pH. In neutral or alkaline solutions, the yellow diperoxo-orthovanadate ion [VO$_2$(O$_2$)$_2$]$^{3-}$ is formed whereas in strongly acidic solutions, red-brown peroxovanadium cation [V(O$_2$)]$^{3+}$
predominates. The yellow “acid salts” KH$_2$[VO$_2$(O$_2$)$_2$].H$_2$O and (NH$_4$)$_2$H[VO$_2$(O$_2$)$_2$].nH$_2$O have been isolated and at 0°, strongly alkaline solution containing an excess of H$_2$O$_2$ deposits blue-violet needles of M$_3$[V(O$_2$)$_4$].nH$_2$O (M = Li, Na, K, NH$_4$).

New Peroxo complexes of vanadium(V) containing some aroylhydrazone ligands having composition Na[VO(O$_2$)$_2$L-L].2H$_2$O (where L-L = BFMH, BTEH, BTMH, BPMH, BAMH and BCMH) have been reported. These complexes have been synthesized by stirring V$_2$O$_5$ with excess of 30% aqueous-H$_2$O$_2$ followed by treatment with methanolic solution of the ligand and finally maintaining the pH of the reaction mixture by adding dilute solution of NaOH (Scheme 2). The complexes have been characterized by various physicochemical techniques, viz., elemental analysis, molar conductivity, magnetic susceptibility measurements, IR, electronic, mass, $^1$H NMR spectral and TGA/DTA studies.$^1$

On the basis of these studies it has been revealed that the complexes are uni-univalent and diamagnetic in nature and thus confirming +5 oxidation state of vanadium. The ligands are bound to metal in a bidentate mode through carbonyl oxygen and azomethine nitrogen. Antifungal activity of complexes revealed enhanced activity of complexes as compared to corresponding free ligands. On the basis of above facts, following structure is proposed for these complexes (Fig. 1).

![Structure of Na[VO(O$_2$)$_2$L-L].2H$_2$O](image)

V$_2$O$_5$ + 4 H$_2$O$_2$ + 2L-L + 2 NaOH $\rightarrow$ 2Na[VO(O$_2$)$_2$L-L].2H$_2$O + H$_2$O

Where, L-L = BFMH, BTEH, BTMH, BPMH, BAMH and BCMH

**Scheme 2: Synthesis of peroxo complexes of vanadium(V) containing some aroylhydrazone ligands.**
A new oxovanadium(V) complex of NH₄VO₃ and tryprophan (TrPH) has been synthesized in aqueous solution at pH 6.0 and characterized by various Physiochemical techniques, viz. elemental analysis, UV-Vis, FT-IR, ¹H-NMR and a mass spectroscopic data. The complex (Na₄[V₃O₉(TrP)]) was diamagnetic in nature as was evident from the electron spin resonance spectroscopy (ESR) and the magnetic susceptibility measurements, in conformity with the presence of vanadium(V) in the structure. The electrochemical behaviour of Na₄[V₃O₉(TrP)] complex was also studied on the hanging mercury drop electrode (HMDE) by using cyclic voltammetry (CV).

Equimolar interaction of VO(OPr)₃ with N-Phenyldiethanolamine (H₂L) affords the dimeric complex [VO(L)(µ-OPr)]₂ (1), (Scheme 3) which on reaction with different glycols yields a new class of oxovanadium(V) complexes of the type: VO(L)(OGOH) (where L = C₆H₅N(CH₂CH₂O)₂ and G = G¹ (CMe₂CH₂CH₂CMe₂) 2, G²(CMeCH₂CMe₂) 3, G³(CH₂CMe₂CH₂) 4, G⁴(CH₂CEt₂CH₂) 5, G⁵(CHMeCH Me) 6 and G⁶(CMe₂CMe₂) 7, featuring N-phenyldiethanolamine and glycolate moieties (Scheme 4). Complexes (2)-(7) react with Al(OPr)₃ to afford novel heterobimetallic coordination complexes of the type: VO(L){(OGO)Al(OPr)²} (G = G¹–G⁶) (Scheme 5). All these complexes have been characterized by elemental analysis and molecular weight measurements. Spectroscopic (IR, UV-Vis and (¹H, ²⁷Al, ⁵¹V) NMR) properties of the new complexes have been investigated and their possible structures have been suggested.

Where C₆H₅=N = PhN(CH₂CH₂O)₂ = L

Scheme 3: Synthesis of dimeric complex [VO(L)(µ-OPr)]₂.
(1) + 2 HOGOH

\[
\begin{align*}
\text{C}_6\text{H}_6 & \quad \text{reflux, 4h} \\
& \quad (-2\text{PriOH})
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{H}_5 & \quad \text{N} \\
& \quad \text{G} \\
& \quad \text{O} \\
& \quad \text{O} \\
& \quad \text{O} \\
& \quad \text{H}
\end{align*}
\]

where \( G = G^1 (\text{CMe}_2\text{CH}_2\text{CH}_2\text{CMe}_2) \) (2); \( G^2 (\text{CHMeCH}_2\text{CMe}_2) \) (3); \( G^3 (\text{CH}_2\text{CMe}_2\text{CH}_2) \) (4); \( G^4 (\text{CH}_2\text{CEtCH}_2) \) (5); \( G^5 (\text{CHMeCHMe}) \) (6); \( G^6 (\text{CMe}_2\text{CMe}_2) \) (7)

**Scheme 4: Synthesis of [VO(L)(OGOH)] complexes.**

\[
\begin{align*}
\text{VO(L)(OGOH)} & \quad + \quad \text{Al(OPr}_i)_3 \\
\text{C}_6\text{H}_6 & \quad \text{Stir, 4h} \\
& \quad (-\text{PriOH})
\end{align*}
\]

\[
\begin{align*}
\text{C}_6\text{H}_5 & \quad \text{N} \\
& \quad \text{G} \\
& \quad \text{O} \\
& \quad \text{O} \\
& \quad \text{O} \\
& \quad \text{Al} \\
& \quad \text{Pr}_i\text{O} \\
& \quad \text{OPr}_i
\end{align*}
\]

\( G = G^1, \, (8); \, G^2, \, (9); \, G^3, \, (10); \, G^4, \, (11); \, G^5, \, (12); \, G^6, \, (13) \)

**Scheme 5: Synthesis of VO(L)((OGO)Al(OPr)_3)_2**

Isovalent \( \mu \)-oxodivaniadium(V) compounds \([\text{L}^1\text{VO(}\mu\text{-O})\text{VO(salen)}]\) (Fig. 2) and its bromo derivative \([\text{L}^2\text{VO(}\mu\text{-O})\text{VO(salen)}]_2\text{CH}_3\text{CN}\) (both \( \text{H}_2\text{L}^1 \) and \( \text{H}_2\text{L}^2 \) are tridentate dithiocarbazate-based ONS ligands) with ligands providing a donor set and coordination number asymmetry have been prepared and characterized from single-crystal X-ray diffraction analysis and NMR. These compounds involve
an octahedral and a square pyramidal vanadium(V) center coupled together by a μ-oxo bridge. An unambiguous description of the coordination geometry around the vanadium centres in these compounds has been obtained through single-crystal X-ray diffraction analysis. An ORTEP view of the complex \([\text{L}^2\text{VO}(\mu-O)\text{VO(salen)})].\text{CH}_3\text{CN}\) clearly depicts that in this complex \(V_1\) is octahedral and \(V_2\) is square pyramidal.

![ORTEP View of Complex](image)

Two neutral dioxovanadium(V) complexes (Fig. 3) having ONS donor sets derived from pyridoxal and S-benzyldithiocarbazate or S-methylthiocarbazate have been prepared by the reaction of vanadyl acetylacetonate and the potassium salts of the ligands in methanol followed by aerial oxidation\(^5\). Equation 1 and 2 represent the synthetic procedure (Scheme 6).

\[
[\text{VO(acac)}_2]+\text{K}_2\text{pydx-sbd} \quad \rightarrow \quad \text{V}^{IV}\text{O(pydx-sbd)} + 2 \text{acac K} \quad (1)
\]

\[
2[\text{V}^{IV}\text{O(pydx-sbd)}] + \text{H}_2\text{O} + 1/2\text{O}_2 \quad \rightarrow \quad 2[\text{V}^{V}\text{O}_2(\text{Hpydx-sbd})] \quad (2)
\]

**Scheme 6: Synthesis of dioxovanadium(V) complexes**

![Scheme 6](image)

**Fig. 3. Structure of dioxovanadium(V) complex**
Their crystal and molecular structures have been determined, confirming the ONS binding mode of the dianionic ligands in their thioenolate form. *In vitro* antiamoebic activities were established for these dioxovanadium(V) complexes.

A wide range of 5-coordinated vanadium(V) alkoxide systems have been investigated. A vanadium(V)alkoxide formed from the reaction of pinacol with VOCl₃ is one of these (Fig. 4). It is used in biological studies modeling the vanadate-ribonuclease complex⁶. This five-coordinate dimer provided an example of characteristic diamond core found in other alkaoxide complexes.

![Fig. 4. A 5-coordinated dimeric vanadium(V) alkoxide complex](image)

The mixed vanadium(V) chloroalkoxides investigated are of interest for their application as catalyst, and their coordination chemistry shows a wide range of geometries with four-, five-, and six-coordinate vanadium(V) in mono and dinuclear complexes with bridged chloro groups⁷ (Fig. 5).

![Fig. 5. Structure of vanadium(V)chloroalkoxide complex](image)

Vanadium(V) forms complexes with a large number of Schiff’s base ligands (Fig. 6). New oxovanadium complexes [VOL(hq)] have been prepared by the reaction of [VO(acac)₂] with ligands LH₂ in the presence of 8-hydroxyquinoline (Hhq). LH₂ is dibasic tridentate ONO mannich base obtained by the reduction of Schiff bases of Salicylaldehyde (Sal) with amino acids; glyine, DL-alanine,
leucine, isoleucine. Spectral studies suggest an octahedral structure for these complexes\textsuperscript{8-10}.

![Fig. 6. Structure of Schiff’s base ligands](image)

Oxo complexes of vanadium(V) with the three amine tris(Phenolate) ligands were easily obtained by the reaction between ligand precursor and VO(O\textsuperscript{iPr})\textsubscript{3} (Fig. 7). The oxo complexes of alkyl bearing ligands could be synthesized by the air oxidation of the corresponding vanadium(III) complexes. These complexes may thus be considered as structural and functional models of vanadium dependent haloperoxidase enzymes\textsuperscript{11}.

![Figure 7: Amine tris(Phenolate) ligands](image)

**OXIDATION STATE (IV)**

Vanadium(IV) forms a number of compounds which includes oxides (VO\textsubscript{2}), halides (VCl\textsubscript{4}) and oxohalides (VOCl\textsubscript{2}). The oxides and the halides are covalent while oxohalides are ionic in character containing the blue VO\textsuperscript{2+} ion. Among the various vanadium(IV) complexes, most widely studied are the VO\textsuperscript{2+} complexes which are the usual products of hydrolysis of other vanadium(IV) complexes.
Vanadyl (VO$^{2+}$) ion is one of the most stable diatomic ions known. VO$^{2+}$ forms stable compounds with F, Cl, O and N donor ligands. These vanadyl complexes are generally green or blue-green and can be cationic, neutral or anionic with the oxoligand along the z-axis of coordination polyhedron e.g., [VO(acac)$_2$], [VO(NCS)$_4$]$^{2-}$ and [VO(bipy)$_2$Cl]$^+$. They are very frequently 5-coordinate with almost invariably square pyramidal stereochemistry and 6-coordinate with distorted octahedral geometry. [VO(acac)$_2$] is the prime example of this geometry (Fig. 8). A sixth ligand may be weakly bonded trans to the V=O to produce a distorted octahedral structure.

Fig. 8. Square pyramidal structure of [VO(acac)$_2$]

In spite of the evident proclivity of VO$^{2+}$ to form square pyramidal or distorted octahedral complexes, it must not be assumed that 5-coordination inevitably result in the square-pyramidal shape. [VOCl$_2$(NMe$_3$)$_2$] is in fact trigonal bipyramidal (Fig. 9).

Fig. 9. The Trigonal bipyramidal Structure of [VOCl$_2$(NMe$_3$)$_2$]
New 1:1 adducts of bis(morpholinedithiocarbamato) complex of VO(IV) with piperdine and morpholine have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility, IR, UV-vis and TGA/DTA techniques. Analytical data reveals that VO(IV) complex forms 1:1 product with the formula [VO(morphdtc)$_2$L]. H$_2$O where L = morpholin and piperdine. Antifungal activity of [VO(morphdtc)$_2$. Morpholine]. H$_2$O has been carried out against the fungal strain Fusarium oxysporium. Thermal study indicates a continuous weight loss. An octahedral geometry has been proposed for 1:1 adducts of VO(IV).

Complexes of oxovanadium(IV) with aldimines, p-chlorobenzophenone-sulfisoxazole, p-chlorobenzophenone-4-aminophenazone, N,N'-dimethyl-p-amino-benzaldehyde-sulfisoxazole, N,N'-dimethyl-p-aminobenzaldehyde-4-amino-2-nitrotoluene, acetophonone-Sulfisoxazole, N,N'-dimethyl-p-aminocinnamaldehyde-sufisomidine, have been synthesized and characterized on the basis of some physicochemical parameters like elemental analyses, molar conductance, magnetic moment, IR spectra and thermogravimetric studies. The molar conductance values of vanadyl complexes in DMSO indicate 1:1 electrolytic nature. The structural studies support square pyramidal geometry of VO(IV) complexes (Fig. 10).

![Structure of VO(C$_{19}$H$_{19}$N$_3$O$_3$S)$_2$(H$_2$O)](image)

**Fig. 10. Structure of [VO(C$_{19}$H$_{19}$N$_3$O$_3$S)$_2$(H$_2$O)]SO$_4$·4H$_2$O**

A series of oxovanadium(IV) complexes with mixed ligands, a tridentate ONO-donor Schiff base ligand [viz., salicylidene anthralinic acid (SAA)] and a
bidentate N,N ligand [viz., 2, 2’- bipyridine (bpy), 1, 10-phenanthroline (Phen), dipyrido [3,2-d: 2’,3’-f]quinoxaline (dpq), dipyrido [3,2-a: 2’,3’-c]phenazine (dppz), or 7-methylidipyrido[3,2-a:2’,3’-c]phenazine (dpdm)] have been synthesized (Scheme 7) and characterized by elemental analysis, electrospray ionization, mass spectrometry, UV-vis spectroscopy, Fourier transform IR spectroscopy, EPR spectroscopy, and X-ray crystallography\textsuperscript{14}. Crystal structures reveal that oxovanadium(IV) is coordinated with one nitrogen and two oxygen atoms from the Schiff base and two nitrogen atoms from the bidentate planar ligands in distorted octahedral geometry (VO$_3$N$_3$). The oxidation state of V(IV) with d$^1$ configuration was confirmed by EPR spectroscopy.

\begin{equation}
\text{OHC OH} + \text{KOH reflux} \rightarrow \text{HC OH} \text{N COOH}
\end{equation}

Scheme 7: Synthesis of Oxovanadium(IV) complexes with a tridentate ONO-donor Schiff base ligand and a bidentate N,N-donor ligand

Oxovanadium(IV) complexes of the type [VO(mac)]SO$_4$ (where mac= tetraaza macrocyclic ligands derived by condensation of furil with 1,4-diaminobenzene or 3,4-diaminopyridine and their reaction with $\beta$-diketones have been prepared using vanadyl ion as kinetic template (Scheme 8). Tentative structures of the complexes have been proposed on the basis of elemental analysis, infrared, e.s.r. and electronic data. All the oxovanadium(IV) complexes are five coordinate\textsuperscript{15}.
Where, $L^1 = \text{Furil} + 1,4\text{-diaminobenzene}$; $L^2 = \text{Furil} + 3,4\text{-diaminopyridine}$

The parent complexes $[\text{VO}(L)]\text{SO}_4$ react with $\beta$-diketones to yield $[\text{VO}(\text{mac})]\text{SO}_4$ as given below:

Where, $\text{mac} = \text{tetraaza macrocyclic ligands derived by condensation of } L^1 \text{ or } L^2 \text{ with } \beta\text{-diketones in presence of oxovanadium(IV) cation}$.

**Scheme 8: Synthesis of $[\text{VO}(\text{mac})]\text{SO}_4$ complexes**

The non-oxovanadium(IV) complexes of composition $[\text{VCl}_2\text{-(acac)}_2\text{(OAr)}_n]$ and $[\text{VCl}_2\text{-(acac)}_2\text{(OAr')}_n] \ [(\text{OAr} = \text{OC}_6\text{H}_4\text{C}_6\text{H}_5\text{-}2; \ \text{OAr'} = \text{OC}_6\text{H}_4\text{C}_6\text{H}_5\text{-}4; \ \text{acac} = \text{acetylacetonate ion (CH}_3\text{COCHCOCH}_3\text{); n = 1 and 2})]$ (Fig. 11) have been reported by the reaction of $[\text{VCl}_2\text{(acac)}_2]$ with the sodium salt of the respective
phenols (Scheme 9). The complexes have been characterized by elemental analyses, molar conductance measurements, molecular weight determinations and infra-red, electronic and FAB-MS spectral and magnetic moment studies. The room temperature magnetic moments of the complexes lying in the range 1.71-1.79 $\mu_B$ conform to V(IV) oxidation state$^{16}$. Based upon these studies, monomeric distorted octahedral structures for the complexes have been proposed.

![Scheme 9: Synthesis of $[\text{VCl(acac)}_2\text{(OAr)}]$ and $[\text{VCl(acac)}_2\text{(OAr')}]$]

![Fig. 11. Structure of non-oxovanadium(IV) complexes]
A new series of 12 complexes of oxovanadium(IV) with hydrazones of isonicotinic acid hydrazide, namely N-isonicotinamido-3',4',5'-trimethoxybenzalidine (INH-TMB) (Fig. 12) and N-isonicotinamido-2'-Furanaldimine (INH-FUR) (Fig. 13) with the general formula VOX₂·nL (X = Cl, Br, I, NCS, NO₃, n = 1; X=ClO₄, n=2; L= INH-TMB or INH-FUR) were synthesized and characterized on the basis of analytical, conductance, molecular weight, magnetic moment, infrared and electronic spectral data. The infrared data of the complexes reveal the bidentate nature of both ligands and coordination to carbonyl-oxygen and azomethinic-nitrogen atoms. The probable coordination number of the central metal is 5 (Fig. 14 and Fig. 15). Thermal stabilities of the complexes were studied through thermogravimetric analysis.

Fig. 12. Structure of N-isonicotinamido-3',4',5'-trimethoxybenzalidine (INH-TMB)

Fig. 13. Structure of N-isonicotinamido-2'-furanaldimine (INH-FUR)

Fig. 14. Structure of VOX₂ (INH-TMB)
Introduction

Synthesis and crystal structure of new oxido[N-(2-oxidobenzylidene-κO) leucinato-κ²N,O](1,10-Phenanthroline-κ²N,N')vanadium(IV) complex having formula [VO(C_{13}H_{15}NO_3)(C_{12}H_8N_2)], has been reported recently\(^\text{18}\). In the title V\(^{IV}\) complex, [VO(C_{13}H_{15}NO_3)(C_{12}H_8N_2)], the oxidovanadium cation is N,N'-chelated by a 1,10-phenanthroline ligand and N,O,O'-chelated by a Shiff base anion in a distorted octahedral geometry i.e. the central V(IV) ion is six-coordinated bound to two O atoms and one N atom of the Schiff base ligand forming a distorted octahedral geometry (Fig. 16).

Several types of Vanadate(IV) compounds are obtained by heating VO\(_2\) with alkaline earth oxides in a high vacuum. These compounds corresponds to the types M\(^{II}\)VO\(_3\), M\(_2\)\(^{II}\)VO\(_4\) and M\(_3\)\(^{II}\)VO\(_5\). Among first row transition metal compounds, Only the vanadyl (VO\(^{2+}\)) ion yields substantial amounts of macrocyclic products\(^9\). The macrocyclic compounds namely vanadyl(IV)corrphycene [(corrph)VO] (Fig.17a) and vanady(IV)10-oxocorrole [(ocor)VO] (Fig.17b) have been prepared and characterized\(^{20-21}\). In both complexes, the V(IV) ion is found in a slightly distorted square-pyramidal
coordination and with almost identical VO bond lengths of 1.587 and 1.585 Å, respectively. The macrocyclic ligands of both these complexes display non-planar distortion modes.

Fig. 17a. Meso-Aryl-Substituted vanadyl corrphycene  Fig. 17b. Vanadyl 10-oxo-corrole

Salen Schiff base complexes of vanadyl (IV) of the type [VO(Chel)] (Fig. 18) where chel = Salen, 5-BrSalen, Me2Salen, 5-MeOSalen, 5-NO2Salen have been prepared and their electrochemical properties have been investigated by cyclic voltametry\(^{22}\). The equatorial Schiff base ligands affect the oxidation potentials via interaction with the d-orbital of the vanadyl metal ion.

\[
\begin{align*}
W &= \text{-CH}_2\text{-CH}_2\text{-} & X &= \text{H, MeO, Br, NO}_2 \\
W &= \text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-} & X &= \text{H, MeO, Br, NO}_2 \\
W &= \text{-C}_6\text{H}_4\text{-} & X &= \text{H, MeO, Br}
\end{align*}
\]

Fig. 18. The Structure of [VO(chel)] Complexes

A vanadium(IV)-oxocorrolazine complex, vanadylotakis(para-tert-butylphenyl) corrolazine, [(TBP)\(_8\)Cz(H)\(^{IV}\)O] (Fig. 19), has been synthesized and characterized by spectroscopic and electrochemical methods. The corrolazine ligand in the complex was shown to contain a labile proton by acid/base Titration and IR spectroscopy, serving as a -2 ligand rather than as the usual -3
The oxidation state of the vanadium center in this complex was shown to be +4, in agreement with the overall neutral charge for this complex. Vibrational spectroscopy provides direct evidence for $V^{IV}=O$ bond through its characteristic stretching peaks in the RR (Resonance Raman) and IR spectra.

A novel oxovanadium complexes with oxazine (Fig. 20a) and with the oxazoline (Fig. 20b) were prepared using VO(acac)$_2$ and their complete characterization done by various techniques such as UV-vis, IR and EPR spectroscopy, mass spectrometry, cyclic voltametry and elemental analysis was reported$^{24}$. In both the complexes, the geometry around vanadium is distorted square pyramidal.

Oxovanadium(IV) complexes of the type $\text{VOL}_2$ are obtained by chelation of vanadium to mixed O,S binding bidentate ligand precursors derived from maltol.
(Fig. 21). These precursor ligands include two pyranthiones, 3-hydroxy-2-methyl-4-pyranthione, commonly known as thiomaltol (Htma) and 2-ethyl-3-hydroxyl-4-pyranthione, commonly known as ethylthiomaltol (Hetma), as well as two pyridinethiones, 3-hydroxy-2-methyl-4(H)-pyridinethione (Hmppt) and 3-hydroxy-1,2-dimethyl-4-pyridinethione (Hdppt). The X-ray structure of oxobis(thiomaltolto)vanadium(IV), VO(tma)$_2$ suggest that both cis and trans isomers were isolated in the same asymmetric unit. In both isomers, the two thiomaltolato lignds are arranged around the base of the square-pyramid with the V = O linkage perpendicular and the vanadium atom is slightly displaced form the basal plane$^{25}$.

\[ R = CH_3, X = O, L^- = tma^- \]
\[ R = C_2H_5, X = O, L^- = etma^- \]
\[ R = CH_3, X = NH, L^- = mppt^- \]
\[ R = CH_3, X = NCH_3, L^- = dppt L^- \]

**Fig. 21. General structure of VOL$_2$ type complexes**

The solid complexes of Oxovanadium(IV) with a new quadridenate ligand (DHACH) derived from 3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione (dehydroacetic acid) and carbohydrazide have been synthesized. The stoichiometry of the complex have been found to be 1:1 (metal: ligand) and have the composition [VO(DHACH)H$_2$O]. DHACH behave as a dibasic quadridentate ligand with O: N: N: O donor sequence towards metal ion and complexes have octahedral stereochemistry (Fig. 22)$^{26}$.

**Fig. 22. Structure of [VO(DHACH)H$_2$O]**
In complexes of oxovanadium(IV)sulphate with hydrazides of cyclobutane, cyclopentane and cycloheptane carboxylic acids and cyclopentylacetic acids, ligands coordinate via the carboxyl O and primary amino N and the sulphate ion is also coordinated in all the complexes\(^{27}\). The reaction of oxovanadium(IV)sulphate with bis(hydrazones)(LH\(_2\)) derived from 1,1'-diacetyferrocene and different aromatic acid/pyridine carboxylic acid hydrazides, in ethanol gives the complex of the type VO(L) (Fig. 23)\(^{28}\).

**Fig. 23. Structure of VO(L) type complex**

**OXIDATION STATE (III)**

Vanadium(III) plays an important role in several environmental systems. The aqueous chemistry of V(III) complexes has been investigated more than any of the oxidation state\(^{29-31}\). Compounds of vanadium are prepared by the reduction of compounds of vanadium with higher oxidation states. Thus, vanadium trichloride, VCl\(_3\), is obtained by the reduction of VCl\(_4\). Vanadium(III) forms a large number of complexes, most of them being anionic. Examples are [V(C\(_2\)O\(_4\))\(_3\)]\(^{3-}\), [V(CN)\(_6\)]\(^{3-}\) and [V(NCS)\(_6\)]\(^{3-}\). A well known example of cationic complex is [V(H\(_2\)O)\(_6\)]\(^{3+}\).

Vanadium(III) complexes of the four mixed O, S donor ligands (Fig. 24) and their corresponding vanadyl(IV) complexes have been reported. The V(III) complexes with pyranthiones, V(tma)\(_3\) and V(etma)\(_3\), were synthesized in good yields (65-79%) from VCl\(_3\) and the respective ligand precursors. The synthesis of vanadium(III) complexes of pyridinethiones, V(mppt) and V(dptt)\(_3\), was also attempted in a fashion analogues to that for V(etma)\(_3\).
The synthesis and complete characterization of vanadium(III) complexes with ligands allomaltol (3-hydroxy-6-methyl-4-pyrone, Hama) and isomaltol [1-(3-hydroxy-2-furanyl)ethanone, Hima] (Fig. 25) has been reported. The complex with allomaltol is tris(allomaltolato)vanadium(III)monohydrate, V(ama)$_3$, while that with isomaltol is tris(isomaltolato)vanadium(III), V(ima)$_3$.

Vanadium(III) complexes of the type [V(Vn$_2$bz)(H$_2$O)Cl$_2$]$_2$ (where Vn$_2$bz = bis(vanillin)benzidine) have been reported. In this complex the ligand Vn$_2$bz has six coordinate sites. The geometry of this vanadium(III) complex is found to be hexacoordinate octahedral. The phenolic OH group and the methoxy groups do not take part in coordination. Only the azomethine nitrogen take part in coordination. Thus, the ligand bis(vanillin)benzidine (Fig. 26) acts as a non-functional bidentate chelating agent. The geometry of this vanadium(III) complex is found to be hexacoordinate octahedral.
OXIDATION STATE (II)

Vanadium forms fairly stable compounds in the oxidation state II. Though stable complexes are formed in oxidation state (II), but this state is least stable as compared to other oxidation states of vanadium. Vanadium(II) complexes are usually prepared by electrolytic or zinc reduction of acidic solution of vanadium in one of its higher oxidation states. Several salts and double sulphates have been prepared and contain \([\text{V(H}_2\text{O)}]_{6}^{2+}\) ion. The adducts \(\text{VCl}_2\) of the type \([\text{VCl}_2\text{L}_4]\), where \(\text{L}\) is one of the number of O- or N-donor ligands, have also been prepared. Other complexes of the type \([\text{VCl}_2\text{L}_2]\) are distinguished by their colour (green) and magnetic moment (~3.2 B.M), well below the spin-only value for three unpaired electrons. They are thought to be halogen-bridged polymers of \(\text{V}^{II}\). \(\text{V}(II)\) is kinetically inert and undergoes substitution only slowly. Some other examples of \(\text{V}(II)\) complexes are \(K_4[\text{V(CN)}]_6\) and \([\text{V(en)}]_3\text{Cl}_2\). Carboxylate derivatives such as trinuclear \([\text{V}_3(\text{RCOO})]_6(\text{Me}_2\text{NCHCHNMMe}_2)\) and binuclear \([\text{V}_2(\text{RNCHCNR})]_4\) [\(\text{R} = \text{P-MeC}_6\text{H}_4\)] have also been prepared\(^{35}\). Complexes like \(\text{VCl}_2(\text{Py})_4\) and \([\text{V(NCS)}]_6]^+\) have octahedral structure. Porphyrin complexes of \(\text{V}(II)\) are also known\(^{36}\).

LOWER OXIDATION STATES

In lower oxidation states, vanadium is capable of forming complexes with bidentate nitrogen donor ligands such as 2,2'-bipyridyl. Tris(bipyridyl) complexes have been prepared by reduction with \(\text{LiAlH}_4\) in THF where the formal oxidation state of vanadium is +1 to -1 e.g., \(\text{V(dipy)}_3^+\), \(\text{V(dipy)}_3\) and \(\text{V(dipy)}_3^-\). In complexes like \(\eta^5\)-\(\text{C}_5\text{H}_5\text{V(CO)}_4\) and \(\text{V(CO)}_2(\text{dmpe})_2\text{Cl}\), vanadium(1) possesses tetragonal pyramidal structure. The zero valent state occurs with \([\text{V(CO)}]_6\) which is a 17-electron species and forms a hydride, \(\text{HV(CO)}_6\), and an anion, \([\text{V(CO)}]_6^-\). The anion reacts with \([\text{NO}][\text{BF}_4]\) to form \(\text{V(CO)}_5(\text{NO})\), an 18-electron system that has an extensive substitution chemistry\(^{37}\). A complex \([\text{V(CO)}]_5]_3^-\) contains vanadium in -3 state.
III. BIOLOGICAL IMPORTANCE OF VANADIUM AND ITS COMPLEXES

Next to molybdenum, vanadium is in fact the most abundant transition metal available in sea water, and this is due to its ability to form easily soluble vanadate under aerobic conditions, where it is present in the form of dihydrogen vanadate, ion-paired with the sodium ions from the salt content of sea water.

The growing interest in vanadium chemistry has been inspired by the discovery of its bioinorganic functions. Vanadium is required for normal health and could act in vivo either as a metal cation or as a phosphate analogue, depending on the oxidation state, V(IV) or V(V), respectively. Vanadium is concentrated in blood cells as the major cellular transition metal. The longest known example of vanadium biochemistry is the accumulation of vanadium in special cells called vanadophores, by certain lower marine organisms called tunicates. In proteins, vanadium is a cofactor in an algal bromoperoxidase and prokaryotic nitrogenases. Vanadium when bound to sulphur donor ligands has drawn considerable attention due to its importance in several biological and industrial processes. Vanadium, may or may not play an important role in normal mammalian metabolism, however, at pharmacological concentration it is already increasing attention as a potential therapeutic agent.

Biologically important role has been assigned to vanadium as an inhibitor of Na+, K+-ATPase and nuclease where V(V) adopted a trigonal bipyramidal geometry on binding to the active site of enzymes. Vanadium participates in enzymatic reaction such as nitrogen fixation by vanadium complexes. Thus, The vanadium dependent nitrogenase enzyme from nitrogen fixing bacteria of the genus azotobactor features vanadium in medium oxidation states of V(II)-V(IV), postulated to bind and reduce dinitrogen. High concentration of vanadium is present in certain ascidians which indicates its specific transport behaviour. The vanadyl complex, amavadin is present in mushroom, Amanita muscarica where it adopts different oxidation states in vivo (Fig.27).
Availability is one important factor for the biological use of an element. Another essential factor arises from the necessity for an organism to employ an element in some kind of processes essential to maintain its metabolism. This condition is again fulfilled for vanadium, since it easily switches between the oxidation states V (in the form of vanadate, $[\text{VO}_4]^{3-}$) and IV (commonly in the vanadyl form, $[\text{VO}]^{2+}$), the two forms of vanadium present in equilibrium in the human body, both permit and complicate various interactions with the biological molecules\(^{46-48}\). The V state is the stable one under aerobic conditions, and IV state under anaerobic conditions, i.e in the cytoplasm. The III state ($\text{V}^{3+}$) is also feasible. Consequently, vanadium thus takes over the role of a cofactor molybdenum, to which there exists a diagonal relationship.

Vanadium is also known to participate in the halogenation of a variety of organic substrates by haloperoxidases. Vanadium as the vanadate ion is an essential prosthetic group of some haloperoxides which are currently being elucidated in great detail\(^{49,50}\). Vanadium ion in the vanadium dependent haloperoxidase (VHPO) enzymes has stimulated interest in biomimetic modes for catalytic halogenation of organic substrates\(^{51}\). Several species of marine algae and a terrestrial lichen contains vanadium haloperoxidases which catalyze the reaction shown in following equation\(^{52}\) (Scheme 10).

$$\text{RH} + \text{H}^+ + \text{X}^- + \text{H}_2\text{O}_2 \rightarrow \text{RX} + 2\text{H}_2\text{O}$$

\[ \text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^- \]

\textbf{Scheme 10}

Interaction of vanadium(IV) and vanadate with proteins provides the key of biological role of vanadium in vivo and in vitro\(^{53}\). Vanadium containing
compounds are used as insulin mimic agents which includes inorganic vanadium salts, complexes resulting from combination of vanadium(V) and hydrogen peroxide and chelated vanadium(IV) complexes. Vanadium may also prove to be useful therapeutic agent for the treatment of various diseases like diabetes, sickle cell anaemia and cancer\textsuperscript{54-56}. In addition to this, a range of other complexes have been examined in tissue culture studies\textsuperscript{57}.

A few metal complexes of VO(IV) with 3,4-methylenedioxy-benzalidene-2-amino-4,5,6,7-tetrahydrobenzothiazole (THMB) have been tested against antibacterial activity of \textit{E. Coil} (gram negative) and \textit{S.aureus} (gram positive) and antifungal activity of \textit{A. niger} and \textit{C. albicans}\textsuperscript{58}. Antifungal screening result shows that [VO(Nfth)H\textsubscript{2}O] is the only complex which has been shown active against \textit{C. kejri} and \textit{C. albicans}\textsuperscript{59}.

Vanadium plays an important, perhaps essential and general role in the regulation of enzymatic phosphorylation. Pharmacological activities of vanadium compounds include insulin enhancing, tumor growth inhibition and prophylaxis against carcinogenesis\textsuperscript{60-62}. Antitumor activity of vanadocene dichloride is comparable to that of cis-platin\textsuperscript{63,64}. Some vanadium complexes are known to inhibit several enzymes including phosphatases ATPases, nucleases, kinases and other enzymes. Vanadium complexes having sulphur functionality have not received much attention, though such complexes have been found to be orally active insulin mimetic agents in the treatment of diabetes\textsuperscript{65-67}.

A new series of transition metal complexes of VO(IV) have been synthesized from the Schiff base (L) derived from 4-aminoantipyrine, 3-hydroxy-4-nitrobenzaldehyde and o-phenylenediamine\textsuperscript{68}. Antimicrobial screening tests gave good results in the presence of metal ion in the ligand system.

Vanadium complexes are well documented to have therapeutic applications. Recent studies showed that oxovanadium complexes of thiourea and vanadium substituted polyoxotungstates exhibit potent anti-HIV properties toward infected immortalized T-cells. However, the instability of vanadium(IV) complexes under physiological conditions has been frequently encountered. To address the
problem in instability, porphyrinato ligand have been employed to stabilize VO\(^{2+}\). Porphyrins have a rigid square planar scaffold which could prohibit the demetalation reaction. The oxovanadium(IV) porphyrins 1a-e (Fig. 28) are stable in GHS containing solutions. Their inhibitory effects on HIV-1(BaL) replication in Hut/CCR5 cells were evaluated. All of these complexes showed anti-viral activities compared to the vehicle control, whereas the water soluble analogue 1a containing aminosulfonyl functional groups exhibited the highest potency at the 5\(\mu\)M level with over 97% inhibition\(^{69}\).

**Fig. 28. Oxovanadium(IV) porphyrin complexes**

HIV-1 reverse transcriptase (RT) is one of the major targets for anti-HIV drugs, and binding of vanadium complexes to RT has been reported. The activity of the oxovanadium(IV) porphyrin 1a toward HIV-1 RT inhibition was measured by
using an ELISA method. Upon treatment of HIV-1 RT in lysis buffer (2ng, 128.7 µl) with 10a (5 and (0% inhibition) 50 µM) dissolved in TBS at 37°C, significant RT inhibition (~38 and 73%, respectively) was observed after 30 minutes incubation compared with the drug-free control.

It has been found that tetrahedral metalloocene complexes containing vanadium(IV) (vanadocene) have spermicidal activity against human sperm. Oxovanadium(IV) complexes with 1,10-phenanthroline, 2,2'-bipyridyl or 5'-bromo-2'-hydroxyacetophenone and their derivatives linked to vanadium(IV) via nitrogen and oxygen atoms have potent spermicidal activity against human sperm. The kinetics of sperm immobilization by the oxovanadium(IV) complexes was dependant on their net charge. Study of different vanadocenes and oxovanadium(IV) complexes demonstrated that the spermicidal properties of these complexes were determined by the oxidation state of the vanadium(IV) atom. The various ancillary ligands linked by either carbon, nitrogen or oxygen atoms to the central vanadium(IV) atom significantly contributed either to the fine tuning of the spermicidal potency or enhancing the stability of these complexes in aqueous solution. The neutral complex of oxovanadium(IV), VO(Br, OH-acph)₂, i.e bromo-hydroxyacetophenone complex rapidly inactivates sperm in seconds. Because this complex was a rapid spermicidal agent, it is likely that this complex is rapidly transported across the sperm cell membranes and because of its rapidity and potency it may be used as contraceptive agent.

The oxovanadium(IV) complexes (I) of the type [VO(L)]SO₄ have been prepared using an in-situ method of synthesis with ligands derived from di-2-thienylethanedione with 1,2-diaminobenzene or 2,3-diaminopyridine. The parent complexes have been further reacted with β-diketones to yield macrocyclic complexes (II) of type [VO(mac)]SO₄ (where mac = macrocyclic ligands derived by condensation of amino group of parent complex with β-diketones), wherein the VO²⁺ cation acts as a template (Fig. 29). Tentative structures for these complexes have been proposed on the basis of elemental analysis, electrical conductance, magnetic moments and spectral (infrared, electronic and electron
spin resonance) data. The oxovanadium(IV) complexes are five coordinated wherein the tetraaza macrocyclic ligands act as tetradebate chelating agents. All the complexes are found to inhibit the infectivity of potato virus X, when checked using the test plant *Chenopodium amaranticolor*.²²

Novel oxovanadium(IV) complexes (1-4) with 2-methyl-3-(pyridine-2-ylmethyleneamino) quinazolin-4(3H)-one (L₁) or 3-(2-hydroxy-3-methoxy benzylideneamino)-2-methylquinololin-4(3H)-one (L₂) were synthesized and characterized by elemental analysis, IR, \(^{1}\)H-NMR, electronic spectra, molar conductance and thermal studies. Based on the above spectral studies, the complexes have the general formula [VO(L₁₂)](1), [VO(L₁)phen](2), [VO(L₂₂)](3) and [VO(L²)phen](4) (Fig. 30). The synthesized compounds were tested for antimicrobial activity by

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<td>Dibenzoylethane</td>
</tr>
</tbody>
</table>

Fig. 29. Structure of [VO(mac)]SO₄, where mac = macrocyclic ligand
disc diffusion method. The results indicate the enhanced activity of metal complexes over their parent ligands. The DNA binding and nuclease activity of the synthesized compounds were also studied. The investigation of the interaction of the complexes with calf thymus DNA has been performed with absorption spectroscopy which showed that the complexes are avid binders of calf thymus DNA. Also the interaction of the oxovanadium(IV) complexes with plasmid DNA was studied using agarose gel electrophoresis. The results revealed that these complexes could act as effective DNA cleaving agents resulting in the nicked form of DNA (\(P_{\text{nc}}\) 19) under physiological conditions\(^{73}\). The gel was run both in the absence and in presence of the oxidizing agent.

![Proposed structures of the complexes](image)

**Fig. 30. Proposed structures of the complexes**

The potential medicinal application such as the treatment of diabetes type I (insulin deficiency) and II (insulin resistance) and anticancer effects has further stimulated research into vanadium coordination compounds\(^{74,75}\). Diabetes is a
mammalian disease in which the amount of glucose in the blood plasma is abnormally high.\textsuperscript{76} The condition can be acutely life-threatening, since patients with diabetes suffer from a number of secondary complications, such as atherosclerosis, microangiopathy, renal disease, cardiac disease, diabetic retinopathy and other vision disorders including blindness. Millions of sufferers control diabetes by daily insulin administration and/or a special diet. Insulin supplementation is the easiest method to control chronic diabetes; however, insulin is not orally active and must be taken by injection. In addition, insulin is essentially inactive in type II diabetes, which is by far the most frequent type of this disease. The development of insulin mimetic compounds for oral amistration would thus be very useful.\textsuperscript{77} In fact, vanadium compounds have a long history as insulin mimetic agents.\textsuperscript{78,79} Vanadium compounds stimulate glucose metabolism without affecting the concentration of insulin. This makes them promising candidates for the treatment of type II diabetic individual (which include the majority of people diagnosed with diabetes) where hyperinsulinemia is of concern because of secondary complications resulting from excess insulin.\textsuperscript{80} Sodium vanadate was reported to have an oral insulin-like effect in human diabetes in 1899. However, it is only in the last decade or so that the pharmacological potential of vanadium has been systematically explored.\textsuperscript{81,82} Aside of vanadium complexes, many other metal compounds, such as derived from molybdenum, tungsten and zinc have been tried, both \textit{in vivo} and \textit{in vitro}, but none rivaled vanadium salts as effective insulin substitutes. A possible reason could tie in the structural resemblance between vanadate and phosphate, which leads vanadium complexes to have the ability either to inhibit the protein tyrosine phosphatase or to activate the insulin receptor kinase and/or glucose carrier, thus triggering glucose intake into cells.

Since 1980, considerable evidence has been provided that vanadium salts, specifically tetravalent vanadyl, usually found as the divalent cation VO\textsuperscript{2+}, and pentavalent vanadate, H\textsubscript{2}VO\textsubscript{4}{-}, have the ability to mimic insulin action in a number of isolated cell systems and to produce dramatic glucose lowering effects when given orally to animal models of both types I and II diabetes.
mellitus\textsuperscript{83,84}. Sodium orthovanadate has been found to stimulate glucose uptake and glucose oxidation in rat adipocytes, stimulate glycogen synthesis in rat diaphragm and liver and inhibit hepatic gluconeogenesis\textsuperscript{85}. A very exciting finding was that vanadate could be administered orally, with a long-term insulin mimetic effect, in vivo. Oral vanadium(V) treatment of diabetic animals partially or completely restored liver and muscle enzyme activities in glycolysis, without stimulating increased insulin synthesis\textsuperscript{86-88}. In addition, it has been shown that oral administration of vanadyl sulphate also lowers blood glucose and blood lipids in STZ (streptozotocin) induced diabetic rats and prevents secondary complications of diabetes such as cataracts and cardiac dysfunction\textsuperscript{89}. The insulin enhancing properties of VO\textsuperscript{2+} and VO\textsuperscript{2+} chelates in diabatic laboratory animals and humans have commanded widespread scientific attention because of the potential for improved therapy through drug design\textsuperscript{90-95}. Although the molecular basis is not known, it is established that the insulin-mimetic action of VO\textsuperscript{2+} chelates, measured as lowering of serum glucose levels in animals or as glucose uptake or lipogenesis in adipocytes, greatly exceeds that of inorganic VO\textsuperscript{2+} \textsuperscript{96-99}. Inorganic vanadium compounds, although they are effective, have poor gastrointestinal absorption and required high doses for therapeutic efficacy\textsuperscript{25}. As far as toxicity is concerned vanadyl ion (VO\textsuperscript{2+}) is superior to vanadate in that it is less toxic.

In consideration of the low intestinal absorption of vanadyl and high toxicity of vanadate (vanadate is an effective inhibitor of many phosphate-metabolizing enzymes); a search for alternative vanadium compounds containing organic ligands has been initiated. The recent successes achieved with organic transition metal complexes suggest that modification of the metal ion chemistry by the organic ligands not only increased efficacy but also decreased toxicity.

Most of the compounds reported contain bidentate ligands and have a 1:2 metal-to-ligand stoichiometry. The typical examples are the vanadyl complexes with maltol and ethylmaltol. Oxovanadium(IV) complexes such as bis(maltato)oxovanadium(IV) (BMOV) and bis(ethylmaltato)oxovanadium(IV) (BEOV) (\textbf{Fig. 31}) are several
times more potent than vanadyl sulphate$^{100}$. VO(malto)$_2$ is prepared nearly quantitatively in water (>90% yield) by combining vanadyl sulphate trihydrate and maltol (3-hydroxy-2-methyl-4-pyrene) (1:2) and it dissolves (mM scale) in a number of organic solvent and water. BMOV has one unpaired electron, characteristic of the vanadyl unit, and a fairly high V=O stretching frequency in the IR (995 cm$^{-1}$), suggesting that there is no ligand (or just weakly bound solvent) in the sixth position. The crystal structure of this compound shows that the two ligands are oriented $trans$ to each other in the base of a square pyramid$^{101}$. BMOV has been shown to have a strong glucose-lowering effect; in the in vivo studies; it is roughly three times more effective than uncomplexed vanadyl (in the form of vanadyl sulphate), with no evidence of toxicity$^{102}$. Both these complexes have the desired properties, namely water solubility, balanced lipophilicity and/or hydrophilicity, neutral charge and thermodynamic stability, for a candidate oral drug.

![Fig. 31. Structure of BMOV and BEOV](image)

A series of complexes with V$^{IV}$O(N$_2$O$_2$) coordination mode have been prepared, in order to study the structure-activity relationship of antidiabetic vanadyl complexes. Among these VO(picolinate)$_2$(VOPA) i.e. bis(picolinato)oxovanadium(IV) (Fig. 32) has been very effective in normalizing the glucose levels of STZ-induced diabetic rats when given intraperitoneally or orally$^{103}$. In the in vivo testing, it has been found that VOPA has modest glucose lowering activity, without accompanying plasma insulin elevation or food intake suppression$^{104}$. 

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Introduction
The insulin-enhancing properties of VO\(^{2+}\) and of VO\(^{2+}\) chelates in diabetic laboratory animals and humans have commanded widespread scientific attention because of the potential for improved therapy through drug design. V-dipicolinate complexes in three different oxidation states (V\(^{III}\), V\(^{IV}\) and V\(^{V}\)) show insulin-enhancing effects in a chronic animal model system (Fig. 33). The thermodynamic stability of the \([\text{V}^{\text{III}}(\text{dipic})_2]^–\) complex was found to be higher than anticipated. The V\(^{V}\)-dipic complex is most effective in lowering blood glucose and suggest that both ligand and metal oxidation states are important for elucidating the action of the complex. Vanadium(V)-dipicolinate is a more potent inhibitor for phosphatases than the corresponding vanadium(V) complexes and is also effective as an oral agent. The compound has been successfully applied orally to diabetic cats.

**Fig. 33. Vanadium dipicolinate complexes**

An additional medicinal aspect with respect to vanadium chemistry is the inhibitory action towards phosphatases not only by simple vanadates, but also by highly condensed form of vanadate, viz. decavanadate; which forms as the pH drops below 6.3. Decavanadates like other polyoxometallates (PMOs) have also
been shown to be potent anti-viral and retroviral agent-leaving apart their importance as redox catalysts in oxo transfer reactions. Many different kinds of POMs have been tested in vivo and in vitro and found to be biologically active. For example, the vanadate dimer $H_2V_2O_7^{2-}$ has been found to be both an inhibitor and an activator for dehydrogenases, isomerases and phosphatases\textsuperscript{105,106}. The vanadate tetramer $V_4O_{12}^{4-}$ inhibits dehydrogenases and aldolases. The vanadate tetramer also appears to be the active species in the photolytically-induced cleavage of myosin at the phosphate binding sites, despite of the fact that the tetramer only has the modest affinity for this protein\textsuperscript{107-110}. Vanadate decamers $H_XV_{10}O_{28}^{(6-x)-}$ show high affinity for selected kinases, phosphorylases and reverse transcriptase, as illustrated by the potent inhibition of phosphofructokinase. Decavandate has previously been used to facilitate crystallization of proteins and the $Ca^{2+}$ transport by ATPase and adenylate kinase\textsuperscript{111,112}.

**IV. GENERAL CHEMISTRY OF NICKEL**

Nickel is a silvery-white lustrous metal with a slight golden tinge. It is one of the four elements that are ferromagnetic around room temperature, the other three being iron, cobalt and gadolinium. Nickel was first isolated and classified as a chemical element in 1751 by Axel Fredrik Cronstedt, who initially mistook its ore for a copper mineral. Its most important ore minerals are laterites, including limonite and garnierite, and pentlandite. The metal is corrosion resistant, finding many uses in alloys, as a plating, in the manufacture of coins, magnets and common household utensils, as a catalyst for hydrogenation, and in a variety of other applications. Enzymes of certain life, forms contain nickel as an active center, which makes the metal an essential nutrient for those life forms. The metal is moderately electropositive and dissolves readily in dilute mineral acids. Nickel can exist in oxidation states -1, 0, II, III, and IV but its only important oxidation state is nickel(II) under normal environmental conditions. Nickel is a transition metal and is hard and ductile. Naturally occurring nickel is composed of 5 stable isotopes; $^{58}\text{Ni}$, $^{60}\text{Ni}$, $^{61}\text{Ni}$, $^{62}\text{Ni}$ and $^{64}\text{Ni}$ with $^{58}\text{Ni}$ being the most
abundant (68.077% natural abundance). The coordination chemistry of nickel spans a wide and interesting variety of coordination numbers, geometries and oxidation states. The principal stereochemistries of Ni(II) are octahedral and square planar. Trigonal bipyramidal, square pyramidal and tetrahedral geometries are also reported. With regard to lewis acidity, Ni(II) is considered to be a borderline metal ion. This is because it binds both soft and hard ligands and sometimes, albeit rarely, to both in the same complex.

V. COMPLEXES OF NICKEL IN DIFFERENT OXIDATION STATES

OXIDATION STATE (IV)

The complexes of Nickel(IV) are all octahedral and diamagnetic with the low spin $t_{2g}^6e_{g}^2$ configuration.

The alkali salts $M_2NiF_6$ made by fluorination are red or Purple and oxospecies like BaNiO$_3$ and $[\text{Ni(Nb}_{12}\text{O}_{38})]^{12-}$ have Ni$^{IV}$. There are some octahedral complexes with phosphine and arsine ligands e.g. $[(\text{diPhos})_2\text{NiCl}_2]^{2+}$ and with dimethylglyoximate $[\text{Ni(dmg)}_3]^{2-}$ that can be made by oxidation of nickel(II) complexes$^{113-116}$.

The crystal structure of Bis[2-(2-aminoethyl)imino-3-butanoneoximato]nickel(IV) Diperchlorate i.e $\text{Ni(C}_6\text{H}_{12}\text{N}_3\text{O}_2)(\text{ClO}_4)_2[-\text{NiL}_2(\text{ClO}_4)_2]$ obtained by oxidation of the parent Ni(II) complex $\text{Ni(HL)}_2(\text{ClO}_4)_2$ with concentrated nitric acid, has been determined from X-ray diffraction data and refined by least square methods$^{117}$. The structure consists of discrete strongly distorted octahedral nickel(IV) complex cations and perchlorate anions. The tridentate ligand is coordinated to the nickel through its nitrogen atoms. HL = 2-(2-aminoethyl) imino-3-butanone oxime ligand.

A series of fourteen octahedral nickel(IV)dithiocarbamato complexes of the general formula $\text{Ni(ndtc)}_3\text{X}_y\text{H}_2\text{O}$ [ndtc stands for the appropriate dithiocarbamate anion, X stands for ClO$_4$ (1-8; $y = 0$) or [FeClO$_4$]$^-$ (9-14; $y = 0$ for 9-12, 1 for 13 and 0.5 for 14] has been prepared by the oxidation of the
corresponding nickel(II) complexes, i.e. [Ni(ndtc)$_2$], with NOClO$_4$ or FeCl$_3$. The complexes involving a high valent Ni$^{IV}$S$_6$ core, were characterized by elemental analysis (C, H, N, Cl and Ni), UV-Vis and FTIR spectroscopy, thermal anlaysis and magnetochemical and conductivity measurements$^{118}$. The X-ray structure of [Ni(hmidtc)$_3$][FeCl$_4$] (9) was determined. It consists of covalently discrete complex [Ni(hmidtc)$_3$]$^+$ cations and [FeCl$_4$]$^-$ anions with slightly distorted octahedral and tetrahedral geometries within the complex cations, and anions, respectively. The Ni(IV) atom is six-coordinated by three bidentate S-donor hexamethyleneiminedithiocarbamate anions (hmidtc) (Fig. 34). Moreover, the formal oxidation state of iron in [FeCl$_4$]$^-$ as well as the coordination geometry in its vicinity was also proved by $^{57}$Fe Mossbauer spectroscopy in [Ni(hmidtc)$_3$][FeCl$_4$].

![Fig. 34. Structure of [Ni(hmidtc)$_3$]$^+$](image)

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<tr>
<td>6,13</td>
<td>bziprdtc ($f$)</td>
<td>benzyl</td>
<td>isopropyl</td>
<td>---</td>
</tr>
<tr>
<td>7,12</td>
<td>Bzmedtc ($g$)</td>
<td>benzyl</td>
<td>methyl</td>
<td>---</td>
</tr>
<tr>
<td>8,14</td>
<td>Chetdtc ($h$)</td>
<td>cyclohexyl</td>
<td>ethyl</td>
<td>---</td>
</tr>
</tbody>
</table>

Schematic representation of the [Ni(ndtc)$_3$]$^+$ complex cation of the nickel(IV) complexes 1-14 given with the list of substituents of the appropriate dithiocarbamate.

The compound, [Ni(C$_5$H$_{10}$NS$_2$)$_3$] [(C$_8$N$_5$)$_3$] i.e Tris(N,N-diethylidithiocarbamato-S,S’)nickel(IV) 1,1,2,3,3pentacyanopropenide which is shown in (Fig. 35) forms a structure with sheets consisting of alternate rows of cations and anions. The nickel atom in the cation has a distorted octahedral geometry. The planar
[C₃(CN)₅]⁻ anion is significantly distorted from C₂ᵥ symmetry. The Ni-S distances range from 2.246-2.257Å and the C-C distances in the allyl group of the anion are 1.19 and 1.35Å.

![Fig. 35. Structure of [Ni(C₅H₁₀NS₂)₃][(C₈N₅)]⁻](image)

**OXIDATION STATE (III)**

There are number of nickel(III) complexes mostly with macrocyclic ligands and peptides. The open-chain ligands such as EDTA⁺ and deprotonated peptides give stable complexes in aqueous solution. The ion [Ni(bipy)₃]³⁺ has an octahedral geometry with tetragonal distortion. The best known compounds in this state are of the type [NiX₃(PR₃)₂] (X = Cl⁻, Br⁻ and I⁻) which have been assigned a trigonal bipyramidal geometry. Tertiary phosphine complexes of this type were the first nickel(III) species to be made by halogen oxidation of NiX₂(PR₃)₂.

With N₂O₂ Schiff-base ligands, Nickel(III) Schiff base complexes and their pyridine adducts have been produced by electrochemical oxidation of nickel(II) complexes derived from naphthaldehyde and identified by EPR spectroscopy (Fig. 36).

![Fig. 36. Ni(III) Schiff base complex](image)

A new coordination compound of nickel with 3,4-toluenedithiole of general formula R[Me(tdt)₂], Me = Ni, R = Pr₄N has been isolated. From Physicochemical measurements follows, that the central nickel is in a formal oxidation state III with coordination number four in square planar arrangement (Fig. 37).
Fig. 37. The arrangement of complex anion \([\text{Ni(tdt)}]_2^-
\)

A novel structurally characterized Ni(III) complex of an N-confused porphyrin inner C-oxide has been synthesized from the oxidation of a Ni(II) N-confused porphyrin using OsO\(_4\). Crystal data: C\(_{53}\)H\(_{40}\)N\(_5\)NiO.CH\(_2\)Cl\(_2\), monoclinic space group P2\(/a\) (No. 13), \(a = 21.229\) (1) Å, \(b = 8.6451\) (5) Å, \(c = 25.762\) (2) Å, \(\beta = 93.004\) (3) \(\gamma = 4721.6\) (5) Å\(^3\), \(Z = 4\) (Scheme 11).

Scheme 11: Synthesis of Ni(III) complex of an N-confused porphyrin inner oxide

Ni(III) dithiocarbamate complexes have also been reported\(^{124}\). Ni(III) dithiocarbamate complexes of the type Ni(S\(_2\)CNHR)\(_2\)X.nH\(_2\)O have been reported (R = Me, Et, Pr, Bu, \(-\text{CH}_2\text{CH}_2\text{OH}\)), m-HOC\(_6\)H\(_4\), cyclohexyl, X = Br, I, ClO\(_4\), n = 0,1,2,). The complexes were prepared by the oxidation of Ni(S\(_2\)CNHR)\(_2\) with Br\(_2\), I\(_2\) or NOCl\(_4\).\(^{125}\) Ni(III) complex with 4-methylpiperazine-1-carbodithioate of the type [Ni(4-Mpipzcdt\(_2\))]\(_2\)ClO\(_4\) have been synthesized and characterized\(^{126}\). The complex was isolated by the oxidation of [Ni(4-Mpipzcdt\(_2\))] with Fe(ClO\(_4\))\(_3\).9H\(_2\)O (Scheme 12).

\[
\text{Ni(4-Mpipzcdt\(_2\)) + Fe(ClO\(_4\))\(_3\) .9H\(_2\)O} \rightarrow \text{[Ni(4-Mpipzcdt\(_2\))]ClO\(_4\) + Fe(ClO\(_4\))\(_2\) .9H\(_2\)O}
\]

Scheme 12
The dtc ligands indeed stabilize the higher oxidation state is very well known. Due to this stabilization, dtc ligands do not tend to be labile and consequently do not detach from their coordinate covalent linkage in the complex Ni(4-Mpipzcdt)$_2$. These complexes are, therefore very stable and it seems difficult for the ligands to form mixture of complexes by interchanging with Fe(III) of Fe(ClO$_4$)$_3$.9H$_2$O. Recently Ni(III) dithiocarbamate complexes of the type [NiL$_2$Cl(H$_2$O)] and [NiLQCL(H$_2$O)], HL = diethylldithiocarbamic acid, HQ = Acetylacetone, Picolinic acid, 8-hydroxyquinoline and DMG were prepared using Cl$_2$ as oxidant. The Ni(III) oxidation state and bidentate coordination of L and Q ligands were confirmed in all the complexes$^{127}$.

**OXIDATION STATE (II)**

Nickel is predominantly bivalent in its compounds. In this oxidation state, nickel atom loses two s-electrons forming nickelous ion, which has pseudo inert gas structure with eight electrons in 3d-orbitals. Nickel in +2 oxidation state exhibits wide and interesting variety of coordination numbers and stereochemistries which often exist simultaneously in equilibrium with each other. The absence of any other oxidation state of comparable stability for nickel implies that compounds of nickel(II) are largely immune to normal redox reaction. Nickel(II) forms a large number of complexes with coordination numbers 3 to 6. The coordination number of nickel(II) rarely exceeds 6 and principal stereochemistries are octahedral and square planar (4-coordinate) with rather fewer examples of trigonal bipyramidal (5-coordinate) and square pyramidal (5-coordinate). Softer ligands such as P and S ligands generally give 4-coordinate species with a strong preference for a square planar geometry. Nickel however, has a tendency to add a further ligand to give 5-coordinate and 6-coordinate compounds. Some complexes of nickel(II) exhibit a coordination number of 3 as in [Ni(NPh$_2$)$_3$]$^{128,129}$. Octahedral complexes of nickel(II) are obtained especially with neutral nitrogen donor ligands such as NH$_3$, en, bipy, phen and oxygen donors such as dimethylsulphoxides (DMSO) and NCS$^-$ and NO$_2$ etc. It is peculiarity of nickel(II) chemistry that complexes of one configuration can be
easily converted to other configurations. This structural lability implies that the free energy difference between different stereochemical forms is usually small. Complexes of nickel(II) with variety of sulphur donor ligands such as dithiophosphates, dithiophosphinates, dithiocarbamates, etc. has been extensively studied.

(a) **FOUR COORDINATED NICKEL(II) COMPLEXES**

Of the four coordinate complexes of nickel(II), those with square planar stereochemistry are the most numerous. They include the yellow [Ni(CN)₄]²⁻, the red bis(N-methylsalicylaldimino)nickel(II). Although less numerous than square planar complexes, tetrahedral complexes of nickel(II) also occur. The simplest of these are the blue [NiX₄]²⁻ (X = Cl, Br, I) ions precipitated from ethanolic solutions by large cations such as [NR₄]⁺, [PR₄]⁺ and [AsR₃]⁺. Other example include a number of those of the type [NiL₂X₂] (L = PR₃, AsR₃, OPR₃, OAsR₃).

Sulphur donor ligands generally give 4-coordinate nickel(II) complexes with a strong preference for square-planar geometry. An important example of such complexes is with a novel tetradentate ligand with NN’OS coordination spheres which was prepared and then the corresponding nickel(II) complex was synthesized (Scheme 13). The ligand and the complex were characterized by elemental analyses, IR and ¹H NMR spectroscopy. The structure of (Methyl 2-(2-((E)-2-hydroxy-5-((E)-P-tildiazenyl)benzyldieneamino)ethylamino)cyclopent-1-ene)carbodithioato)nickel(II) has been determined by X-ray crystallography. The X-ray results confirm that the geometry of the complex is slightly distorted square-planar structure. The nickel(II) ion coordinate to two nitrogen atoms from the imine moiety of the ligand, a sulphur atom from the methyl dithiocarboxylate moiety and a phenolic oxygen atom.
Scheme 13: General synthesis of (Methyl-2-(2-((E)-2-hydroxy-5-((E)-Para-tildazenyl)benzylideneamino)ethylamino)cyclopent-1-ene-carbodithioate)nickel(II)

A series of complexes with general formula MLX₂ [where M = Co and Ni; X = Cl; L = 2-(2-Pyridyl)benzimidazole ligands] have been synthesized and characterized by elemental analysis and ¹H NMR spectroscopy. The complexes have square planar geometry and were prepared in two steps. Treatment of these complex with methylaluminoxane (MAO) leads to active catalysts for ethylene oligomerization for the olefins from C₄ to C₆ as oligomers (Scheme 14)¹³³.

Scheme 14: Procedure for the formation of MLX₂ where M = Ni and Co; R₁ = R₂ = H or CH₃.

Complexes of type Ni(SSiMe₂R₂)(dPpe) [R = Me, n-Bu] were prepared by the treatment of (C₅H₅)₂TiCl₂ and NiCl₂(dPpe) with the corresponding lithium silanethiolates. The complex readily reacted with (C₅H₅)TiCl₃ to produce the Ti-Ni heterobimetallic compound (C₅H₅)TiCl(μ-S)₂Ni(dPpe), in which silicon-sulphur bond cleavage takes place (Scheme 15). These complexes have been characterized by spectroscopic techniques and elemental analysis. X-ray structural data for the complex has also been reported¹³⁴.
Scheme 15: Synthesis of (C₅H₅)TiCl(μ-S)_2Ni(dPPe), dPPe=1,2-bis(diPhenylphosphino)ethane.

A nickel(II) complex with 1,2-dithiolate ligand, [Ni(tfadt)_2]^1/-2^- has been synthesized (Fig. 38). The preparation, electrochemical properties and X-ray crystal structures of the square planar nickel complexes, in both their dianionic diamagnetic [Ni(tfadt)_2]^2^- and monoanionic paramagnetic [Ni(tfadt)_2]^1^- forms were reported as η-Bu₄N^+, PPh₄^+ and (18-crown-6)Na^+ salts respectively.

![Fig. 38. The square planar structure of [Ni(tfadt)_2]^1/-2^-](image)

**FIVE COORDINATED NICKEL(II) COMPLEXES**

Five coordination is rather unusual in nickel(II) complexes. Some of the square planar complexes have a tendency to add further ligand to give five coordinated complexes. The essential condition required for the formation of five coordinated nickel(II) complexes is its stereochemical nature. The ligand must be such that the bulk and deposition of its part allow only five coordinating centres to approach the central metal ion closely. If the ligand is polydentate, any five coordinating complexes it forms will have an additional stability due to its structural rigidity.

A series of new coordination compounds with composition [Ni(cetdtc)(triphosII)]X (where cetdtc = cyclohexylethyldithiocarbamate; dtc = S₂CN¯; X = Cl¯, PF₆^-, BPh₄^- and ClO₄^-; triphosII = C₄H₃P₃=1,1,1-tris(diphenylphosphinomethyl)ethane) and [Ni(Pe₂dtc(triphosII))]X (X = Cl¯, ClO₄^- have been synthesised. The isolated complexes have been characterized by elemental analysis, IR and UV-visible spectroscopy, thermal analysis, magnetochemical and conductivity...
measurements. All complexes are diamagnetic, 1:1 electrolytes, with pentacoordinated nickel in the NiS₂P₃ chromophore (Fig. 39).\textsuperscript{(47)}

![Predicted structure for the complexes [Ni(R₁R₂dtc)(triPhosII)]X (R₁ = Cyclohexyl, Pentyl; R₂ = ethyl, Pentyl; X = Cl⁻, PF₆⁻, BPh₄⁻, ClO₄⁻).](image)

A thiocyanate-bridged dinuclear nickel(II) complex having the composition \([\text{Ni}_2(\text{C}_{11}\text{H}_{11}\text{Br}_2\text{N}_2\text{O})_2(\text{NCS})_2]\) has been synthesized. The asymmetric unit contains two molecules. Both nickel atoms in each molecule have a square pyramidal coordination geometry and each center is bound by one oxygen atom and two nitrogen atoms of one Schiff’s base ligand and by one nitrogen atom from the bridging thiocyanate ligand, which define the basal planes nitrogen atoms from the bridging thiocyanate ligands occupy apical position (Fig. 40).\textsuperscript{(138-143)}

![Proposed structure of [Ni₂(C₁₁H₁₁Br₂N₂O)₂(NCS)$_{2}$] complex.](image)

New 1:1 adducts of bis(morpholinedithiocarbamato) complexes of nickel(II) with piperdine and morpholine have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility, IR, UV-vis and
TGA/DTA techniques. Analytical data reveals that Ni(II) forms 1:1 diamagnetic adducts having general formula Ni(morphdtc)_2L (where morphdtc = morpholinedithiocarbamate; L = morpholine and piperidine). Antifungal activity has been carried out against the fungal strain Fusarium oxysporium. A square pyramidal geometry has been proposed for these complexes\textsuperscript{12}.

**SIX COORDINATED NICKEL(II) COMPLEXES**

Ni(II) forms octahedral complexes with the maximum coordination number of 6. The octahedral complexes are often prepared in aqueous solution by replacement of coordinated water with the neutral or anionic ligands. These complexes are characteristically blue or purple in contrast to the bright green colour of hexaaquanickel(II) ion. On treatment of aqueous solutions of nickel(II) thiocyanate with alkali metal thiocyanate solution, green hydrated complex salt like K\textsubscript{4}[Ni(NCS)\textsubscript{6}].4H\textsubscript{2}O is obtained in which nickel is octahedrally coordinated.

The complex of formula [Ni(NH\textsubscript{2}CH\textsubscript{3}CHCOO)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}].2H\textsubscript{2}O has been prepared from nickel(II) chloride in aqueous solution by adding DL-alanine and potassium hydroxide. It has been crystallized from aqueous solution and its structure was determined by X-ray structure analysis, i.r, and uv-visible spectroscopy. The molecular structure shows that the complex is a chelate with two N,O-coordinating bidentate alanime ligands and two water molecules\textsuperscript{144}. The complex is neutral and dehydrated. The coordination polyhedron is an octahedral with trans arrangement of the equal ligands. The complex has an inversion center at the nickel(II) ion (Fig. 41).

![Structure of \[Ni(NH_2CH_3CHCOO)_2(H_2O)_2\]2H_2O](image)

A series of mixed ligand complexes having the general composition [M(L)(en or Phen)X\textsubscript{2}] (where M = Ni(II), Co(II) or Mn(II); L = 2-Phenyl-3-(benzylamino)-1,2-dihydroquinazolin-4(3H)-one; X = N\textsuperscript{3+} or NCS\textsuperscript{-}) (Fig. 42) have been
prepared and characterized by Physico-chemical, spectroscopic and thermal studies. On the basis of spectral studies octahedral geometry has been proposed. The Phen complexes Fig. (a) are more stable than en complexes Fig. (b). The electrochemical behaviour of the Ni(II) complexes showed that the complexes of Phen are reduced at more positive potential compared to the corresponding en complexes\textsuperscript{145}.

![Fig. 42. Proposed structure of [M(L) (en or Phen)X\textsubscript{2}] where M = Ni(II), Mn(II) and Co(II), L=2-Phenyl-3-(benzylamino)-1,2-dihydroquinazolin-4(3H)-one and X = N\textsubscript{3} and NCS\textsuperscript{−}.](image)

A six coordinated Ni(II) complex having composition [Ni(CH\textsubscript{3}COO)\textsubscript{2}(3,5-lutidine)\textsubscript{2}(H\textsubscript{2}O)\textsubscript{2}] has been synthesized and characterized by X-ray structural analysis and IR spectra. The Ni(II) assumes the distorted octahedral geometry and is bound with two nitrogen atoms of the two crystallographically equivalent lutidine ligands, two oxygen atoms of monodentate acetate ions and with two water molecules. The nitrogen atoms of two lutidine molecules are in axial position and the oxygen atom of water molecules and the acetate ions in equatorial position. The neutral complex interact through the O–H\ldots O hydrogen bonds with water molecules as the proton donors and non coordinated acetate oxygen atom as the acceptor (Fig. 43)\textsuperscript{146}.
Introduction

Fig. 43. Structure of $[\text{Ni(CH}_3\text{COO)}_2(3,5\text{-lutidine})_2(H_2O)_2]$%

Complexes of the type $[\text{MPy}_2(\text{dedtc})_2]$ and $[\text{MPy}_2(\text{dpdtc})_2]$, where $M = \text{Mn(II)}, \text{Fe(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and $\text{Zn(II)}$, have been synthesized (Scheme 16). These complexes have been characterized on the basis of elemental analysis, magnetic susceptibility TGA/DSC and infrared in the solid and electronic spectroscopy and conductivity measurement studies in solution. The dithiocarbamato moiety has been found to symmetrically bonded to the metal. The complexes are proposed to have a distorted octahedral structure$^{147}$. 

Scheme 16: Synthesis of the complexes $[\text{MPy}_2(\text{dedtc})_2]$, where $M = \text{Mn(II)}$, $\text{Fe(II)}$, $\text{Co(II)}$, $\text{Ni(II)}$, $\text{Cu(II)}$, $\text{Zn(II)}$, $\text{Py} = \text{C}_5\text{H}_5\text{N}$ and $R = \text{C}_6\text{H}_5$ or $\text{C}_8\text{H}_5$. 

\[ \text{R} \quad \text{N} \quad \text{S} \quad \text{SNa} \quad \text{R} \quad \text{N} \quad \text{S} \quad \text{SNa} \quad \text{M} \quad \text{Cl} \quad \text{Cl} \quad -2\text{NaCl} \]
OXIDATION STATE (I)

Nickel (I) complexes are binuclear and diamagnetic with a total of eight ligands, although one with only six is also known.

In (I) oxidation state, the complex formed has tetrahedral geometry with coordination number four. The majority of nickel(I) complexes contain phosphine ligands and have tetrahedral or trigonal bipyramidal geometries e.g \( \text{Ni(PPh}_3\text{)}_2X \) or \( \text{Ni(PPh}_3\text{)}_2X_2 \) [where \( X = \text{Cl}^-\), \( \text{Br}^-\) and \( \text{I}^-\)]. The reduction of nickel(I) halides with NaBH\(_4\) in ethanol has been studied in the presence of various tertiary phosphines and arsines. Complexes of the type XNiL\(_3\) have been isolated in this way when \( X = \text{Cl}^-\), \( \text{Br}^-\) and \( \text{I}^-\) and \( L = \text{PPh}_3\), \( \text{AsPh}_3\), no reaction being observed when \( L = \text{PET}_3\), \( \text{PBu}_3\) and \( \text{Ph}_2\text{P(CH}_2\text{)}_2\text{PPh}_2\). The reaction of XNiL\(_3\) with CO gas at room temperature produces pentacoordinate carbonyl complexes XNi(CO)\(_2\)L\(_2\), when \( L \) is triphenylphosphine. The lack of stability prevents the isolation of similar complexes when \( L \) is triphenyl arsine\(^{148-151}\).

The catenand cat-30 forms a \( d^9 \) nickel(I) complex by electroreduction of the nickel(II) precursor, \( \text{Ni(cat-30)}^{2+} \); owing to the particular arrangement of the coordinating subunits and to the special topology of the ligand, the nickel(I) complex displays exceptional redox stability\(^{152}\).

LOWER VALENCY STATES (-1), 0

Nickel in the lower oxidation state -1, 0 and 1 is encountered in complexes involving \( \pi \)-bonding ligands. Ni(-1) is found in the carbonyl anion \([\text{Ni}_2(\text{CO})_6]^{2-}\). In oxidation state zero, the complexes of coordination number 2, 3, 4 and 5 have been reported. Oxidation state zero is found in complexes having CO or PR\(_3\) ligand e.g \([\text{Ni(CN)}_2(\text{CO})_2]^{2-}\). Most nickel(0) cyanide complexes such as \([\text{Ni(CN)}_4]^4-\) and \([\text{Ni(CN)}_2(\text{CO})_2]^{2-}\) are also well characterized.
New olefinic complexes of zerovalent nickel containing 2,2-dimethyl-1-methylenecyclopropane and 1,3,3-trimethylcyclopropene as ligands and stabilized with triphenylphosphine have also been synthesized\textsuperscript{153-155}.

\[\text{[Ni(CO)\textsubscript{4}]}\] is best known carbonyl complex and it is tetrahedral volatile, very poisonous, easily oxidized and flammable. It is reduced by sodium in liquid ammonia to give carbonyl hydride \[\text{[Ni(CO)\textsubscript{3}H\textsubscript{2}]}(\text{NH\textsubscript{3}})\textsubscript{4}\]. This is red coloured and is dimeric. A phosphine derivative \[\text{[Ni(PF\textsubscript{3})\textsubscript{4}]}\] and mixed compounds such as \[\text{[Ni(CO)\textsubscript{2}(PF\textsubscript{3})\textsubscript{2}]}\] are also known\textsuperscript{156}.

Another interesting complex in which the nickel(0) is three coordinated is all trans-1,5-9-cyclododecatrienеникел(0), C\textsubscript{12}H\textsubscript{18}Ni. This compound is the only known nickel(0) complex in which the nickel atom is coordinated only to three olefinic double bonds. X-ray analysis shows that the nickel atom sits at the centre of the ring with a planar trigonal hybridization; Ni-CH distance is about 2.11Å as in (\textbf{Fig. 44})\textsuperscript{157}.

\begin{figure}[h]
\centering
\includegraphics[width=0.3\textwidth]{trans159cyclohexatrienienickel0.png}
\caption{\textbf{Trans-1,5,9-cyclododecatriene nickel(0)}}
\end{figure}

The reduction of the Ni\textsuperscript{1} species \[\text{[Ni\textsubscript{2}(\mu-C\text{Me})\textsubscript{3}(PPh\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})\textsubscript{2}]} [PF\textsubscript{6}\textsubscript{2}](1) with sodium amalgam leads to the formation of the complex \[\text{[Ni\textsubscript{2}0(\mu-C\text{Me})\textsubscript{2}(PPh\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})\textsubscript{2}]}\] (2), the crystal and molecular structure of which has been determined. The molecular structure of (2) displays unusual Cis, Cis bridging diphosphine ligands. The bridging C\text{Me} ligand of the complex is very basic and can be easily protonated by weak acids to form \[\text{[Ni\textsubscript{2}0(\mu-C\text{MeH})\textsubscript{2}(PPh\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2})\textsubscript{2}]} [PF\textsubscript{6}]\) (3), the crystal structure of which also has been determined\textsuperscript{158}.

The tetrakis(phenylisocyanide)nickel(0) complexes \[\text{[Ni(CNR\textsubscript{4})]}\] R = C\textsubscript{6}H\textsubscript{5}, 1; R = C\textsubscript{6}H\textsubscript{3}-2,6-Me\textsubscript{2}, 2; R = C\textsubscript{6}H\textsubscript{4}-2-NO\textsubscript{2}, 3) have been synthesized\textsuperscript{R}. Complex 1-3

\textit{Introduction}
were characterized by X-ray diffraction. All the complexes contain a nickel atom which is coordinated in a slightly distorted tetrahedral fashion\textsuperscript{159} (Fig. 45).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{tetakisPhenylisocyanideNickel0_complexes.png}
\caption{tetakis(Phenylisocyanide)nickel(0) complexes.}
\end{figure}

VI. BIOLOGICAL IMPORTANCE OF NICKEL AND ITS COMPLEXES

Although not recognized until the 1970’s nickel plays important roles in the biology of microorganisms and plants. Nickel is an essential cofactor of enzymes found in eubacteria, archaebacteria, fungi and plants\textsuperscript{160-165}. In these organism nickel is involved in enzymes that catalyze both non-redox (e.g. urease, glyoxalase I) and redox (e.g. hydrogenase, carbon monoxide dehydrogenase and superoxide dismutase) reactions\textsuperscript{166} and proteins involved in the transport, storage, metallocenter assembly, and regulation of nickel concentration have evolved. Studies of structure/function relationships in nickel biochemistry reveal that cysteine ligands are used to stabilize the Ni(III/II) redox couple\textsuperscript{167}. Certain nickel compounds have also been shown to be potent human carcinogens. A likely target for carcinogenic nickel is nuclear histone proteins.

Nickel complexes occur in several nickel-containing enzymes which have been proposed to be involved in catalytic reactions. Nickel containing enzymes are well known in the bacterial world. Currently, seven microbial nickel-containing enzymes have been identified including urease, hydrogenase, Carbon monoxide
dehydrogenase (CODHs), methyl coenzyme M reductase, Ni-superoxide dismutase (NiSOD), glyoxylase I, and cis-trans isomerase. Bacteria with nickel containing enzymes represent a good model to study nickel biometabolism, transport systems and nickel-binding proteins\textsuperscript{168}.

Hydrogenase enzymes catalyze the formation of hydrogen gas from protons and electrons and/or reverse reaction. Methyl-coenzyme M reductase contains a prosthetic group consisting of a redox-active NiN\textsubscript{4} macrocycle (factor F\textsubscript{430}) (Fig. 46)\textsuperscript{169}. It catalyses the reduction of methyl-coenzyme M (CH\textsubscript{3}-SCoM) and coenzyme B (HS-CoB) to methane and the corresponding heterosulphide CoM-S-S-CoB in the final step in methane biosynthesis.

Another enzyme CODHs catalyses the reversible conversion of carbon monoxide and water to carbon dioxide and 2[H]. There are two types of CODHs, those containing molybdenum\textsuperscript{170} and those containing nickel. MoCODH occurs only in aerobic bacteria, whereas the NiCODH is only found only in anaerobically growing microorganisms, both bacteria and archaea\textsuperscript{171}.

Nickel-containing superoxide dismutase (NiSOD) has been isolated from several \textit{Streptomyces}. NiSOD is the newest member of a group of enzymes (superoxide
dismutase) that are responsible for the protection of cell from superoxide\textsuperscript{172,173}. The superoxide radical is a by product of aerobic metabolism, which if not eliminated may cause significant cellular damage and has been implicated in numerous medical disorders\textsuperscript{174}. Some reported examples include [Ni(BH)\textsubscript{3}(H\textsubscript{2}O)(NO\textsubscript{3})(ClO\textsubscript{4})] and [Ni(BH)\textsubscript{2}(NO\textsubscript{3})\textsubscript{2}] which have been proven to be efficient catalyst for the dismutation of superoxide in alkaline DMSO-NBT (Nitro blue tetrazolium chloride). A number of octahedral nickel(II) complexes with tri/tetradentate ligands have been reported having superoxide dismutase activity\textsuperscript{175}.

It has been reported that water soluble Ni(II) complexes with dinitrogen aromatic ligand effect the structure and conformation of DNA. One such complex with composition [Ni(bipy)\textsubscript{2}(phen-dione)](OAc)\textsubscript{2}.2H\textsubscript{2}O (Fig. 47) has been synthesized and characterized by physico-chemical and spectroscopic methods. Binding studies of this complex with calf thymus DNA (CT-DNA) were studied by electronic absorption spectroscopy, Fluorescence spectroscopy, circular dichroic spectral and viscosity measurements. In fluorimetric studies, the enthalpy and entropy of the reaction between the complex and CT-DNA showed that reaction is exothermic\textsuperscript{176}.

![Fig 47. Structure of [Ni(bipy)2(phen-dione)](OAc)2H2O complex](image)

In view of the antimicrobial activity of heterocyclic Schiff’s base ligand bis(2-(pyridine-2-ylimino)phenyl)-4,4’-(diazone-1,2-diyl)dibenzoate (BPPDL), metal complex with Ni(II) has been synthesized and characterized (Fig. 48). The ligand and its complex were tested for the antibacterial activities towards
bacteria *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative) and antifungal activities towards fungi *Aspergillus niger* and *Candida albicans*. The results show that the complex has more antibacterial activities than ligand\(^1\)\(^7\)\(^7\).

![Proposed structure of \([ML]^{2+}\) where \(M = \text{Ni(II)}, \text{Zn(II)}, \text{Co(II)}\) and \(Cu(II)\) and \(L = \text{BPPD}\)](image)

**Fig. 48. Proposed structure of \([ML]^{2+}\) where \(M = \text{Ni(II)}, \text{Zn(II)}, \text{Co(II)}\) and \(Cu(II)\) and \(L = \text{BPPD}\)**

A series of nickel(II) mixed ligand complexes of some disubstituted dithiocarbamates with ethylsalicylaldiminate have been synthesized and characterized. The complexes have general formula, \([\text{Ni(EtSal)}(R_2\text{dtc})]\) where EtSal = ethylsalicylaldiminate, \(R_2 = \text{dibenzyl(Bz}_2\), \text{di-iso-butyl(i-Bu}_2\), \text{di-n-butyl(n-Bu}_2\), \text{ethylbutyl(EtBu)}\, \text{methylbutyl(MeBu)}\, \text{Methylphenyl(MePh)}\, \text{cyclohexylmethyl(C-HxMe)}\), and dtc = dithiocarbamate. The complexes show selective activity against three microorganisms - *proteus mirabilis*, *candida tropicalis* and *candida pseudotropicalis* and selective inactivity against four others, *Escherichia Coli*, *staphylococcus aureus*, *Pseudomonas aeruginosa* and *candida glabrata*\(^1\)\(^7\)\(^8\). Generally, the complexes show moderate antimicrobial activity which is independent of the solvent used.

Nickel(II) complexes with bis(acetophenone)ethylenediamine(acphen) and 5-chloro or bromosalicylideneaniline (HSB) have been prepared and characterized on the basis of elemental analysis, thermogravimetric analysis, magnetic measurements, electronic and IR spectra. The antimicrobial activity of the ligands, metal salts and their corresponding complexes was tested against
Salmonella typhi (bacteria), Saccharomyces cerevisiae (yeast), and two fungal species Lasiodiplodia theobromae and Fusarium oxysporum (Fig. 49)\(^{179}\).

![Diagram of bis(5-chloro or bromosalicylideneaniline)(acphen)Ni(II) (X=Cl, Br)](image)

**Fig. 49. Schematic structure of bis(5-chloro or bromosalicylideneaniline)(acphen)Ni(II) (X=Cl, Br)**

**VII. BIDENTATE SULPHUR LIGAND SYSTEMS**

Bidentate sulphur ligand systems include 1,1-dithiolates, 1,2-dithiolates and 1,3-dithiolates which forms four membered, five membered and six membered chelate ring complexes with substantial electron delocalization respectively.

**1,1-dithiolates:** Four membered chelate complexes are formed when two sulphur donor atoms are linked to the same carbon atom as shown in the (Fig. 50).

![Diagram of 1,1-dithiolates](image)

**Fig. 50.**

Bifunctional CH acids of the type H\(_2\)CXY reacts with CS\(_2\) in presence of a base to give either dithioacids or 1,1-ethylenedithiolate. The reaction is thought to proceeds by the mechanism shown below (Scheme 17)\(^{180}\).

![Scheme 17](image)
Where X, Y are electron withdrawing groups, B is the base

Scheme 17: Proposed mechanism for the formation of 1,1-dithiolate compounds

The structure of four membered chelate ring complexes containing 1,1-dithiolato systems are given in (Fig. 51).

![Diagram of four-membered chelate ring complexes](image)

The 1,1-dithioacids are readily obtained by the addition of uninegative nucleophiles to CS₂ under different experimental conditions. The addition of dinegative nucleophiles gives rise to dinegative 1,1-dithiolates. A number of metal complexes containing 1,1-dithiolato systems forming four membered chelate rings are reported

1,2-DITHIOLATES

These bidentate sulphur ligand systems form five membered unsaturated chelate rings upon complexation when two sulphur atoms are linked to adjacent carbon atoms (Fig. 52).
The most important parent ligands are cis-1,2-disubstituted ethylene dithiolates and benzene-1,2-dithiolates, whose complexes are generally referred to as dithiolenes or dithiones (Fig. 53). These form a wide variety of monomeric and a smaller group of dimeric bis-chelate species.

All known \([\text{M-S}_4]^2-\) complexes are apparently monomeric, but exclusive formation of \([\text{M-S}_4]^+\) monomer is restricted to those species derived from the ligands which do not bear strongly electron withdrawing substituents\(^\text{183}\).

1,3-DITHOLATES

Dithioacetylacetone, 1,3-dithiolate ligand function as bidentate ligand via sulphur atoms forming six membered chelate ring complexes (Fig. 54)\(^\text{184}\).

Apart from the bis complexes of metal ions, tris(dithioacetylacetonato) complexes of some metal ions have also been prepared. These include iron(II), ruthenium(III) and osmium(III) complexes of dithioacetylacetone having the...
general formula \([\text{M(sacsac)}_3] \) (Fig. 55) where \(\text{M} = \text{Cr}^{\text{III}}, \text{Fe}^{\text{III}}, \text{Ru}^{\text{III}}\) and \(\text{Ir}^{\text{III}}\). The tris chelates are neutral low-spin monomers\(^{185}\).

![Diagram of M(sacsac)₃ complex](attachment:image.png)

**Fig. 55**

**VIII. GENERAL INTRODUCTION TO XANTHATES**

Xanthates also called O-alkyl or aryldithiocarbonates are one of the interesting member’s of the 1,1-dithiolate family. These have been extensively used in classical and organometallic chemistry. Xanthate usually refers to a salt with the formula \(\text{ROCS}_2\text{M}^+\) (\(\text{R} = \text{alkyl or aryl group; } \text{M}^+ = \text{Na}^+, \text{K}^+ \text{ etc.})\). The name xanthates is derived from the greek word (xanthous) meaning yellow. Xanthates salt are produced by the reaction of an alcohol with sodium or potassium hydroxide and carbondisulphide\(^{186-188}\) (Scheme 18).

\[
\text{ROH} + \text{CS}_2 + \text{MOH} \rightarrow \text{RO(C=S)SM} + \text{H}_2\text{O}
\]

Where \(\text{R}\) stands for an alkyl hydrocarbon

\(\text{M}\) denotes a monovalent metal such as Na or K.

**Scheme 18: General Synthesis of alkali metal xanthate**

The reaction most probably involves nucleophilic addition of the alkoxide ion to the carbon disulphide molecule. A variety of alcohols have been xanthated in this manner and the chemistry of xanthated ligand has been reviewed and studied extensively. Some commercially important xanthate salts include Sodium ethylxanthate (\(\text{CH}_3\text{CH}_2\text{OCS}_2\text{Na}\)), Potassium ethyl xanthate (\(\text{CH}_3\text{CH}_2\text{OCS}_2\text{K}\)), Sodium
isopropylxanthate \(((\text{CH}_3)_2\text{CHOCS}_2\text{Na})\), Sodium isobutyl xanthate \((\text{C}_4\text{H}_9\text{OCS}_2\text{Na})\) and Potassium amyl xanthate, \((\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OCS}_2\text{K})\).

Metallic derivatives of \(\text{ROCS}_2^-\) ligands have been known since 1857 when these were first prepared by W. C. Zeise, who also termed them as xanthates, a name derived from the Greek word xanthous (yellow), owing to the yellow colour of copper xanthates. Other names for xanthates include xanthogenates, carbodithioates, O-alkylidithiocarbonates and sodium or potassium salts of xanthic (or dithiocarbonic) acids. From the time of discovery by Zeise until the beginning of 19\(^{th}\) century, xanthates found no commercial application. Shortly after 1900, the rubber industry used xanthates in curing and vulcanization of rubber. Later the use of xanthates in the manufacture of synthetic textiles and as fungicides was also observed.

Xanthates are the salts and esters of xanthic acid \(\text{ROC}(=\text{S})\text{SH}\); which are essentially dithiocarboxylic acid or O-ester of dithiocarboxylic acid where \(\text{R}\) is an alkyl or aryl group. These are thus called as dithiocarbonates. The two oxygen atoms in carbonic acid are replaced by sulphur and one hydrogen atom by an alkyl group to obtain xanthic acid

\[
\begin{align*}
\text{O}\equiv\text{C}<\text{OH} & \quad \text{S}\equiv\text{C}<\text{OR} \\
\text{Carbonic acid} & \quad \text{Xanthic acid}
\end{align*}
\]

In xanthic acid, hydrogen atom can be easily replaced by a metal ion. If it is replaced by another alkyl group, it will form dialkyl xanthates i.e.,

\[
\text{S}\equiv\text{C}<\text{OR}
\]

The free xanthic acid are pale yellow unstable oils, and are generated from corresponding alkali metal salts by acidification of dilute sulphuric acid. The alkali metal xanthate salts are obtained directly upon xanthation and although a great number of these have been prepared and characterized. The most
interesting reaction of these salts is their pyrolysis to form olefins. The general reaction for the synthesis of potassium ethyl xanthate is (Scheme 19):

\[
\text{CS}_2 + \text{KOH} \rightarrow \text{S} = \text{C} \overset{\text{SK}}{\underset{\text{OH}}{\text{O}}}
\]

\[
\text{S} = \text{C} \overset{\text{SK}}{\underset{\text{OH}}{\text{O}}} + \text{EtOH} \rightarrow \text{S} = \text{C} \overset{\text{SK}}{\underset{\text{OEt}}{\text{O}}} + \text{H}_2\text{O}
\]

Scheme 19: Synthesis of \(\text{CH}_3\text{CH}_2\text{OCS}_2\text{K}\)

The second step is slow and is thus rate determining. The crystal structure of potassium ethyl xanthate has been determined.

Xanthates can function either as unidentate or bidentate chelating ligands as shown below (Fig. 56).

In the chelating mode, they frequently stabilize the metal centre in an unusually high apparent formal oxidation state. They are capable of stabilizing transition metals in a wide range of oxidation states.

The xanthate ion can be represented in the following three canonical forms: (Fig. 57):

\[
\text{R} \overset{+}{\overset{\text{O}}{\text{O}}} \overset{+}{\overset{\text{C}}{\text{C}}} \overset{+}{\overset{\text{S}}{\text{S}}}
\]

(I)

\[
\text{R} \overset{0}{\overset{\text{O}}{\text{O}}} \overset{0}{\overset{\text{C}}{\text{C}}} \overset{0}{\overset{\text{S}}{\text{S}}}
\]

(II)

\[
\text{R} \overset{0}{\overset{\text{O}}{\text{O}}} \overset{0}{\overset{\text{C}}{\text{C}}} \overset{0}{\overset{\text{S}}{\text{S}}}
\]

(III)

Fig. 57. Resonance forms of xanthate ion
In ionic compounds, the structure is represented by canonical form (I) Fig. 57. In this structure $\pi$-bond character of $\text{C}=\text{S}$ will be lowered, while the $\sigma$-bond of $\text{C}–\text{O}$ will acquire a partial $\pi$-bond character and this results in lowering of the $\text{C}–\text{S}$ frequency and an enhancement of the $\text{C}–\text{O}$ frequency. In covalent compounds, xanthate structures are represented by (II) and (III) and no bonding is expected between metal atom and the $\pi$-bonded sulphur atom.

The decomposition of solid xanthates is enhanced by the action of heat. The products reported among the thermal decomposition of xanthates are dixanthogens, alcohols, elemental sulphur, dialkylxanthates, mercaptans, mercaptides and metallic sulphide.

The decomposition of xanthate is of much greater interest largely because of its importance in mineral flotation. On dissolution xanthates dissociate, forming cations of alkali metals and xanthate anions. Although they are strong electrolytes, in the solution they undergo slow hydrolysis giving rise to xanthic acid, which further decompose into carbon disulphide and alcohol (Scheme 20).

$$\text{RO–C=S} + \text{H}_2\text{O} \rightarrow \text{RO–C=SH} + \text{OH}^-$$

$$\text{RO–C=SH} + \text{H}_2\text{O} \rightarrow \text{CS}_2 + \text{ROH}$$

**Scheme 20**

The decomposition would be enhanced by lowering the pH of the solution to neutralize the $\text{OH}^-$ ions produced. In presence of oxygen, xanthate is oxidized to dixanthogen according to the reaction (Scheme 21).

$$2 \text{S=C=O} + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{S=C=S=O} + 2\text{OH}^-$$

**Scheme 21**
Various mild oxidizing agents such as iodine and hydrogen peroxide are effective in bringing out this reaction. However, dithanthogens are readily reduced to xanthate by the nascent hydrogen generated in alkaline medium by the action of a metal such as zinc (Scheme 22).

\[
\text{Scheme 22}
\]

\[
\begin{align*}
\text{S} &= \text{C} - \text{S} - \text{S} - \text{C} = \text{S} + 2\text{H} + 2\ \text{NaOH} &\rightarrow &\ 2\ \text{S} - \text{C} - \text{SNa} \ + \ 2\ \text{H}_2\text{O} \\
\text{OR} & & &\text{OR}
\end{align*}
\]

In neutral or mild alkaline solutions the following reaction occurs (Scheme 23).

\[
\text{Scheme 23}
\]

\[
\begin{align*}
6\ \text{S} - \text{C} &\rightarrow 6\ \text{ROH} + \text{CO}_3^{2-} + 3\text{CS}_2 + 2\text{CS}_3^{2-} \\
\text{OR} & &
\end{align*}
\]

In strong alkaline solutions, the following main reaction occurs (Scheme 24)

\[
\text{Scheme 24}
\]

\[
\begin{align*}
\text{S} &= \text{C} - \text{S} - \text{C} = \text{S} + 5\text{OH}^- &\rightarrow &\ 2\text{S}^{2-} + \text{CO}_3^{2-} + \text{ROH} + 2\text{H}_2\text{O} \\
\text{OR} & & &
\end{align*}
\]

The decomposition of xathates in an alkaline medium is very slow. The higher the concentration and temperature of the solution the more intense the decomposition of xanthate. The rate of decomposition of xanthates is also influenced by the length of the hydrocarbon chain. Higher homologues of xanthates are less rapidly decomposed in water than lower ones. However, the decomposition of xanthate in alkaline medium results in the formation of monothiocarbonate as an intermediate by replacement of the double-bonded

\[
\begin{align*}
\text{C}_2\text{H}_5\text{O} &\rightarrow \text{C} - \text{S} - \text{O} + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \\
\text{KS} & &\text{KS}
\end{align*}
\]
sulphur atom by oxygen and the sulphur is oxidized to sulphate at the expense of hydrogen peroxide according to the following reaction (Scheme 25).

**Scheme 25**

Monoalkyl xanthates (I) are rapidly hydrolysed in dilute acid and the rate limiting step is a spontaneous heterolysis of undissociated acids (II). The zwitter ion (III) may be an intermediate formed in low concentrations, or a proton transfer from sulphur to oxygen could be concerted with C-O bond breaking\(^{189,190}\) (Scheme 26). The protonated ester (IV) is formed at low pH and is unreactive unless the group R can be eliminated readily as a carbocation.

\[
\text{RO} = \text{CS}_2 + \text{H}^+ \xrightarrow{\text{(I)}} \text{ROCS}_2\text{H} \quad \text{R} = \overset{\text{O}^+}{\text{O}^-}\text{CS}_2 \quad \text{H}^+ \quad \text{H}^+ \quad \text{[ROCS}_2\text{H}_2]^+ \quad \text{ROH} + \text{CS}_2 \quad \text{(IV)} \quad \text{(V)}
\]

**Scheme 26**

Alkali metal xanthates are pale yellow solids in the pure form and have a faint odour. When kept in the atmosphere, a deeper yellow colour and a rather unpleasant odour resembling that of carbon disulphide is observed. This is due to slow decomposition of xanthates in the atmosphere and the product of decomposition; especially organosulphur compounds cause the disagreeable odour even when present in lower concentration.

Xanthates of alkaline metals such as calcium, strontium, and barium are less soluble than that of potassium and sodium xanthates, but they are comparatively strong electrolytes and are prepared by the reaction of an alcohol, CS\(_2\) and metal
hydroxide in the stoichiometric ratio of 2:2:1 with the elimination of water according to the reaction (Scheme 27).

\[ 2\text{ROH} + 2\text{CS}_2 + \text{M(OH)}_2 \rightarrow 2\text{H}_2\text{O} + (\text{ROCS}_2)_2\text{M} \]

\[(\text{M} = \text{Ca}, \text{Sr or Ba}; \text{R} = \text{Me}, \text{Et or Pr})\]

**Scheme 27**

Xanthates of group III elements such as thallium, indium and gallium have been described. They are formed as practically insoluble precipitates on mixing potassium xanthate with an equivalent quantity of nitrate solution of group III elements. The xanthates of main group elements have been less studied as compared to the xanthates of transition elements. However, considerable work has been done on xanthates of tin and germanium\textsuperscript{191-193}.

The first successful synthesis of a variety of metal aryl xanthates has been reported by the reaction of carbon disulphide with phenol in presence of metal\textsuperscript{194-196}.

**IX. XANTHATES OF TRANSITION METALS**

The chemistry of transition metal xanthates has attracted much interest for their importance in the field of metalloenzymes, material precursors metallurgy and catalysts\textsuperscript{197}.

Xanthates of a large number of transition metal such as Cr, Mn, Fe, Co, Ni, Cu, Zn, Ag, Mo etc. are known. Since they are sparingly soluble in water they are obtained by precipitation following the double decomposition of a solution of sodium or potassium xanthate and a soluble salt of the heavy metal. The precipitation and filtration should be carried out in nitrogen atmosphere since heavy metal xanthates in the moist state are very susceptible to decomposition in the presence of oxygen and carbon dioxide.

Xanthates of vanadium were formed by the reaction of sodium metavanadate with the potassium xanthates at pH 5-6 gives VO[S\textsubscript{2}COR\textsubscript{3}] (R = CH\textsubscript{3} or C\textsubscript{2}H\textsubscript{5}). A
simple synthetic procedure leading to the $V_2(S_2)_{2}(RPCS_2)_4$ species ($R = \text{Et or } ^1\text{Pr}$) has also been developed. X-ray structure of $V_2(S_2)_{2}(EtOCS_2)_4$ has also been reported\textsuperscript{198}.

The synthesis of methyl and ethyl xanthate complexes of platinum(II), palladium(II), nickel(II), chromium(II) and cobalt(II) have also been described. The Platinum(II) xanthate complex can be obtained by the reaction of aqueous solution of Potassium chloroplatinate with aqueous solution of potassium xanthate. The complex is bright yellow in colour, diamagnetic in nature. Palladium(II) xanthates are prepared by the similar reaction procedure, substituting $K_2\text{PdCl}_4$ for $K\text{PtCl}_6$. These are also found to be diamagnetic\textsuperscript{199} with the following structures (**Fig. 58**).

![Diagram](image)

*Where $M = \text{Pt, Pd and } R$ is an alkyl group*

**Fig. 58**

Zinc ethyl xanthate is not precipitated in solution but can be prepared by careful crystallization because of its higher solubility. Zinc amyl xanthate and the higher homologs can be prepared by precipitation. They are white in appearance. Zn(II) complexes of general formula $[\text{Zn}(S_2\text{COEt})_2L]$ [$L = \text{Pyrazole (HPZ)}_1$; 3,5-dimethylpyrazole (HdmPz)$_2$; 2-pyridylamine (Pyam)$_3$; Phenyl 2-Pyridylamine (PhPyam)$_4$; 2,2'-dipyridylamine (dPyam)$_5$; 1,4-pyrazine (Pyr)$_6$] have been synthesized and characterized by elemental analyses, IR and NMR spectroscopy. The crystal structures of 2,5, and 6 have been determined by X-ray diffraction, showing different geometries and modes of coordination of the xanthate ligand depending on the type of N-donor ligand\textsuperscript{200}.

A xanthate complex of molybdenum with the formula $\text{Mo}_2\text{O}_3(\text{CS}_2\text{OC}_2\text{H}_5)_4$ (**Fig. 59**) has been studied in detail employing single crystal X-ray diffraction method\textsuperscript{R}. It consists of two distorted octahedron sharing an oxygen atom so as to
form a linear Mo-O-Mo group. There is second oxygen atom on each molybdenum atom adjacent to the bridging one and the remaining four atoms bound to each molybdenum atom are xanthate sulphur atoms. In this structure, molybdenum exists both in tetravalent as well as in hexavalent states. Such a structure also explains the intense colours of the solution of the complex and the metallic appearance of their crystals\textsuperscript{201,202}.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{structure.png}
\caption{Structure of Mo$_2$O$_3$(CS$_2$OC$_2$H$_5$)$_4$}
\end{figure}

The complex is found to be diamagnetic nature.

New oxo complexes of composition MO(S$_2$COR)$_2$(PMe$_3$) ($M = Mo$ or $W$ and $R = Me$, Et or i-Pr) have been synthesized by the reaction of MOCl$_2$(PMe$_3$)$_3$ with the potassium O-alkylxanthates in THF at room temperature. The NMR spectra of the complexes indicate the existence of two isomers in solution, which are proposed to differ in the orientation of the PMe$_3$ and OR groups with respect to the Mo=O group (Fig. 60)\textsuperscript{203}.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{isomers.png}
\caption{Two isomeric structure of MO(S$_2$COR)$_2$(PMe$_3$)}
\end{figure}
Xanthates of copper have attracted considerable attention because of the variable oxidation state of copper. A soluble xanthate reacts with Cupric salt to form Cupric xanthate according to the following reaction, which is brown in colour. The reaction involved is (Scheme 28).

\[
\text{Cu}^{2+} + 2\text{S} \equiv \text{C} \equiv \text{S}^+ \xrightarrow{\text{K}^+} \text{Cu} \left[ \begin{array}{c} \text{S} \equiv \text{C} \equiv \text{S} \\ \text{OC}_2\text{H}_5 \end{array} \right]_2 + 2\text{K}^+ \\
\text{Cupric ethyl xanthate}
\]

Scheme 28

Being unstable, it changes rapidly to cuprous xanthate of intense yellow colour according to the following reaction (Scheme 29).

\[
2\text{Cu} \left[ \begin{array}{c} \text{S} \equiv \text{C} \equiv \text{S} \\ \text{OC}_2\text{H}_5 \end{array} \right]_2 \xrightarrow{} 2 \left[ \begin{array}{c} \text{S} \equiv \text{C} \equiv \text{SCu} \\ \text{OC}_2\text{H}_5 \end{array} \right] + \text{S} \equiv \text{C} \equiv \text{S} \equiv \text{C} \equiv \text{S} \\
\text{Cuprous ethyl xanthate} \\
\text{Diethyl dixanthogen}
\]

Scheme 29

Dixanthogen is simultaneously produced. The dixanthogen is then extracted with benzene or diethyl ether and cuprous xanthate is obtained in pure state.

Potassium 1,3-bis(N-methylpiperazino)propan-2-O-xanthate (LK) and its complexes with Co(II), Ni(II) and Cu(I) ions have been prepared and characterized as [CoL₂(H₂O)₂], [NiL₂(H₂O)₂]2H₂O and CuL. 2H₂O by FT-IR, ¹H, ¹³C NMR spectroscopies and found to have following structures (Fig.61). L = 1,3-bis(N-methylpiperazino)propane-2-O-xanthate.
Introduction

The luminescent Copper(I) complex \([(\text{PPh}_3)_2\text{Cu(S}_2\text{COMe})]\) (Fig. 62) has been obtained by treating \([(\text{PPh}_3)_2\text{Cu(NO}_3])\] with carbon disulphide in a mixed solvents of methanol and dichloromethane at room temperature. The copper has been found to exhibit photoluminescence behaviour at room temperature. The structure of the complex has been determined by X-ray structural analysis\(^{205}\).

![Structure of \([(\text{PPh}_3)_2\text{Cu(S}_2\text{COMe})]\)](image)

Each copper atom has a CuP\(_2\)S\(_2\) tetrahedron coordination skeleton.

The crystal and molecular structure of the compound, \([\text{Ni(phen)}_2(\text{CH}_3)_2\text{CHOCS}S]^+ (\text{CH}_3)_2\text{CHOCS}S^-\) (Fig. 63) has been determined by X-ray diffraction. The brown crystal is triclinic of space group P1, with parameters a = 11.790 (2), b = 12.410(3) c = 12.680(3)Å, \(\alpha = 92.49(3)\), \(\gamma = 117.43(3)\)° and Z = 2. The compound contains a six-coordinate cation and an isopropyl xanthate anion \((\text{CH}_3)_2\text{CHOCS}S^-\), the central Ni atom is chelated by four nitrogen atoms of two phenanthroline ligands and two sulphur atoms of an isopropyl xanthate ligand. The TG data indicate that it decomposed completely at 734 °C\(^{206}\).
A linear polymeric complex, \{[\text{Ni}(\text{C}_{11}\text{H}_{17}\text{OS}_{2})_2(\text{C}_{10}\text{H}_8\text{N}_2)]_2.2\text{CHCl}_3\}_n\} has been reported (Fig. 64). The asymmetric unit in the complex comprises two Ni atoms, each situated on a two fold axis, half each of two 4,4'-bipyridine ligands, each with its long axis aligned on a two fold axis, two xanthate (S_2\text{COC}_{10}\text{H}_{17}) ligands and two CHCl_3 molecules. The Ni atom is octahedrally coordinated by a trans-N_2S_4 donor set, with the N atoms provided by bridging 4,4'-bipyridine ligands and S atoms from two chelating xanthate ligands\(^\text{207}\).

The complex \textit{trans}-Bis(O-ethylthiocarbonato-S,S')bis(isoquinoline) nickel(II) has been reported. The nickel atom in the title compound, \[\text{Ni}(\text{C}_2\text{H}_5\text{OCS}_2)_2(\text{C}_9\text{H}_7\text{N}_2)_2\], (Fig. 65) has a distorted octahedral coordination. It lies on a two fold axis in the plane formed by the four S atoms of the two chelating ethylxanthates. The two isoquinoline ligands occupy apical sites\(^\text{208}\).
Some mixed ligand complexes of nickel(II) with O-butyldithiocarbonate as a primary ligand and substituted pyridines as secondary ligands have been isolated and characterized on the basis of analytical data, molar conductance, magnetic susceptibility, electronic and infrared spectral studies. The molar conductance studies show their non-electrolytic behavior. Magnetic and electronic spectral studies suggest octahedral stereochemistry around Ni(II) ions. One of the
adducts bis(O-butyldithiocarbonato)bis(3,5-dimethylpyridine)nickel(II) has been characterized by X-ray crystallographic studies\textsuperscript{209}. The dithiocarbonates of manganese corresponding to Mn(S\textsubscript{2}COEt\textsubscript{n} (n = 2 or 3) and their adducts with nitrogen donor ligands were conveniently obtained\textsuperscript{210}. High-spin mixed ligand Mn\textsuperscript{2+} complexes of the type Mn(S\textsubscript{2}COR\textsubscript{2}L where R= i-C\textsubscript{3}H\textsubscript{7}, i-C\textsubscript{4}H\textsubscript{9}, [L=1,10-phenanthroline (Phen), 2,2’-bipyridyl (2,2’-Bipy), 4,4’-bipyridyl (4,4’-Bipy)] have been synthesized. As solid the compounds are stable to oxidation by atmospheric oxygen. An X-ray structural study of the [Mn(S\textsubscript{2}COC\textsubscript{3}H\textsubscript{7}-i)\textsubscript{2}(2,2’-Bipy)] complex was carried out. The structure is composed of discrete monomeric molecules. The coordination polyhedron of the Mn atom is a distorted [4S + 2N] octahedron. The molecules are bonded by vander wall’s interactions\textsuperscript{211}. Monomeric, five coordinated bis(ethylxanthato)Zn\textsuperscript{II}(phosphine) complexes [phosphine=PPh\textsubscript{3}, P(o-tolyl)\textsubscript{3}, P(CH\textsubscript{2}Ph)\textsubscript{3}] have been synthesized. The characterization of all the compounds has been carried out by elemental analysis and spectroscopic methods (IR and NMR)\textsuperscript{212}. The complexes have been synthesized by the addition of the phosphine ligand (1:1 molar ratio) to CH\textsubscript{2}Cl\textsubscript{2} solutions of [Zn(S\textsubscript{2}COEt)\textsubscript{2}] (Scheme 31).

\[
\begin{align*}
[Zn(S_{2}COEt)_{2}] + L & \rightarrow [Zn(S_{2}COEt)_{2}L] \\
L &= \text{PPh}_3, \text{P(o-tolyl)}_3, \text{P(CH}_{2}\text{Ph})_3
\end{align*}
\]

Scheme 31

Bidentate ligands Ph\textsubscript{2}PCH\textsubscript{2}CH\textsubscript{2}PPh\textsubscript{2} (dppe) and Ph\textsubscript{2}P(CH\textsubscript{2})\textsubscript{4}PPh\textsubscript{2}(dppb) reacted in 1:2 molar ratio to form dinuclear phosphine bridged complexes (Scheme 32).

\[
\begin{align*}
2[Zn(S_{2}COEt)_{2}] + L-L & \rightarrow [(S_{2}COEt)_{2}Zn(\mu-L-L)Zn(S_{2}COEt)_{2}] \\
L - L &= \text{dppe}, \text{dppb}
\end{align*}
\]

Scheme 32

The Zn-P bonds are very labile and are probably broken in solution.
The structure of binuclear $[(S_2COEt)_2Zn(\mu-dppb)Zn(S_2COEt)_2]$, as determined by X-ray crystallography, shows a distorted trigonal bipyramidal environment for the Zn atoms, formed by two chelating xanthates and bridging dppb ligand.

Many of the transition metal xanthates form complexes with pyridine and other nitrogen donors. Ferric xanthates form a complex in which molar ratio of pyridine to ferric xanthate is 3:1 when dried. The crystals loose pyridine in air reverting back to ferric xanthate. Nickelous and zinc xanthates form coordination complexes with 2 moles of pyridine but these are less stable than that of iron. Cuprous xanthate forms a 1:1 complex. Xanthates of mercury and lead form no complexes.

The reaction of pyridine with tris(O-methylxanthato) iron(III), tris(O-ethylxanthato)iron(III) leads bright yellow complexes which have magnetic moments, isomeric shifts and large quadrupole splitting values indicative of dipyridinobis(xanthato)iron(III) complexes\textsuperscript{213}.

The $[\text{Cd}(\text{C}_5\text{H}_5\text{N})_2(S_2\text{CO}-\text{n-}C_4\text{H}_9)_2]$ adduct of $[\text{Cd}(S_2\text{CO}-\text{n-}C_4\text{H}_9)_2]_n$ with pyridine was synthesized and characterized by IR, elemental analysis, $^1\text{H}$ NMR and X-ray diffraction analysis. The complex has a centrosymmetric structure as shown in Fig. 67\textsuperscript{214}. The complex demonstrates to have non linear optical properties.

![Fig.67. $[\text{Cd}(\text{C}_5\text{H}_5\text{N})_2(S_2\text{CO}-\text{n-}C_4\text{H}_9)_2]$](image)

The synthesis and characterization of gold(I) complexes of butyl xanthate $[\text{Au}_2(^n\text{Bu-xanthate})_2]$, and ethyl xanthate $[\text{Au}_2(\text{Et-xanthate})_2]$, have been
SYNTHESIS AND CHARACTERIZATION OF SOME XANTHATE COMPLEXES OF METALS OF 3d TRANSITION SERIES AND THEIR ADDUCTS WITH NITROGEN AND OXYGEN DONORS

Introduction

described (Fig. 68). The two xanthates complexes are characterized by $^1$H NMR, IR, mass spectrometry, elemental analysis, and UV-Visible techniques. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) show that the gold xanthate complexes decompose to yield mainly gold metal at ~200°C, confirmed by X-ray powder diffraction. The dinuclear gold(I) xanthate complex, \([\text{Au}_2(\text{n-Bu-xanthate})_2]\), is the first structurally characterized binary Au(I) xanthate$^{215}$. The dimer gold(I)xanthate complex \([\text{Au}(\mu_2\text{S}_2\text{COBu})_2]\) crystallizes in orthorhombic space group as green plates.

\[ \text{OR} \]
\[ \text{S}_2 \text{Au} \text{S}_2 \text{OR} \]
\[ \text{Au} \]
\[ \text{OR} \]

Fig. 68. Dinucleargold(I) xanthate; \( R = \text{Et, n-Bu} \)

A series of triorganophoshine gold(I) xanthates \([\text{(R}_3\text{P})\text{Au}(\text{S}_2\text{COR})]\) complexes have been prepared and characterized spectroscopically. Based on crystallographic evidence, the molecules feature linear gold(I) geometries defined by sulphur and phosphorus donors. The complexes along with a series of known anti-cancer agents have been screened against a panel of seven human cancer lines$^{216}$.

A yellow coloured complex dimethyl(2,6-dimethylphenylxanthato)gold(III) has been prepared by the reaction of potassium 2,6-dimethylphenylxanthate and \([\text{(CH}_3\text{)}_2\text{AuI}]_2\) in nitrogen atmosphere. The structure of the complex has been elucidated$^{217,218}$ (Fig. 69).

\[ \text{CH}_3 \]
\[ \text{Au} \]
\[ \text{CH}_3 \]
\[ \text{CH}_3 \]
\[ \text{S} \]
\[ \text{C} \sim \text{O} \]
\[ \text{CH}_3 \]
\[ \text{CH}_3 \]

Fig. 69. Yellow complex dimethyl(2,6-dimethylphenylxanthato)gold(III)
Introduction

X. APPLICATIONS OF XANTHATES

Metal dithio complexes have been extensively investigated because of their combination of functional properties, specific geometries, and molecular interactions that confer them an enormous interest in the field of magnetism, conductivity and non linear optics\textsuperscript{219-221}. These complexes display unconventional electrical and magnetic properties that include ferromagnetism, metallic and superconducting properties. 1,1-dithiolato systems involving sulphur donor ligands are of current interest due to their potential biological activity and practical applications in the field of rubber technology and agriculture. They have been successfully used as fungicides, pesticides, vulcanization accelerators, floatation agents and high pressure lubricants\textsuperscript{181,222-227}. Moreover, these complexes show rich thermal and photochemical behavior\textsuperscript{228,229}. In comparatively recent work, these have been considered for sensing and purification applications and have been incorporated into a variety of magnetic and conducting materials\textsuperscript{230-232}.

As far as metal xanthates are concerned, these are extensively used as pharmaceuticals, fungicides, pesticides, rubber accelerators, corrosion inhibitors, agricultural reagents and quite recently in therapy for HIV infections\textsuperscript{233,234}.

Metallic xanthates are well known reagents in the floatation of minerals of transition metals such as copper, zinc, cobalt and, nickel, and in the separation and quantitative determination of a large number of cations\textsuperscript{235-237}. A unique use of alkali metal xanthates is in the removal of metallic mercury from contaminated industrial land sites. Metal-complexes have low solubility products and high stability constants, and therefore xanthates exhibit high efficacy for removal of ions. Moreover, xanthates possess the desired heteropolar structure.
comprising a hydrocarbon chain and the polar group (S=C=\(\overline{\text{S}}\)) that has a potent effect on a large number of sulphide minerals. As a result, xanthates function as efficient collectors for sulphide minerals which can thus be separated from gangue matter. Xanthates have been found to be particularly effective for galena, pyrite, and chalcopyrite, and in the presence of certain modifying agents they are almost used for the entire family of sulphide minerals. An important use of xanthates is the selective beneficiation of galena (PbS) and sphalerite (ZnS)\(^{238}\).

Zinc xanthates are active catalysts in stereoregular polymerization of propylene oxide. They are markedly more stable than that of known classical stereoregular catalysts in this field. But the steric control of zinc xanthates is weaker. Zinc butyl xanthate has been used as an accelerator in vulcanization of rubber. These have also been used in protection of rubber against atmospheric gases especially oxygen and ozone\(^{239}\).

With the purpose of finding more effective catalyst systems, the xanthates of Cu, Pb, Ni, Fe, Al and Sn are investigated. Among these, only copper isopropyl xanthate (Cu(i-Pr)\(\text{Xt}\)) and tin isopropyl xanthate (Sn(i-Pr)\(\text{Xt}\)) were appeared to be active.

Effects of two typical surfactants, Tween-80 and sodium isobutyl-xanthate (NaIBX), with different concentrations on the growth and sulphur-oxidizing activities of a new strain Acidithiobacillus albertensis BY-05, an acidophilic sulphur-oxidizing bacterium, were investigated. The results indicate that both surfactants can enhance the growth and sulphur-oxidizing activities of A. albertensis BY-05 only at some special concentrations, e.g., \(10^{-4}\)-\(10^{-8}\) g/L for NaIBX and lower than \(10^{-8}\) g/L for Tween-80, but were inhibited and even harmful at higher concentrations. Both surfactants can not be metabolized by A. albertensis BY-05. The contact between the bacteria and the sulphur particles may be dependent upon both the extracellular substance and the surfactants, both of which provide the amphiphilic environment improving the attachment for bacteria to the sulphur particles surface. These data could be significant for enlarging the applications of both A. albertensis BY-05 and some typical surfactants for industrial bioleaching of sulphide minerals\(^{240}\).
Extensive studies over the past 20 years have focused on the biological properties of xanthate derivatives. Xanthates have recently been shown to inhibit the replication of both DNA and RNA viruses in vitro. The antiviral activity was exerted only under acidic pH conditions. Certain members of xanthate family were shown to be potent antiviral and antitumor agents. It was postulated that xanthates exert these effects by their ability to selectively inhibit phospholipase C, to stimulate tumor necrosis, and to inhibit angiogenesis.

The success as well as the limitations of cisplatin as an antitumor agent prompted investigation of other metals. Antitumor complexes with yttrium (Y), titanium (Ti), vanadium (V), molybdenum (Mo), technetium (Tc), rhenium (Re), iron (Fe), ruthenium (Ru), osmium (Os), cobalt (Co), rhodium (Rh), iridium (Ir), nickel (Ni), palladium (Pd), copper (Cu), gold (Au), and bismuth (Bi) were described.

Recently, a platinum complex based on sulphur as complex forming, atoms, bis(ethylxanthato)platinum(II) named thioplatin, with antitumor activity against a number of human tumor lines was described (Fig. 70).

![Fig. 70. Structure of Thioplatin](structure.png)

It was found that thioplatin displayed significant higher toxicity when tumor cells were cultivated in media of pH 7.4. because in solid tumors a pH of 6.8 or lower has been frequently observed, an improved therapeutic index with thioplatin has been expected.

![Bis(isopropylxanthato)platinum(II)](structure.png)

![Bis(O(1-ethyl)propylxanthato)platinum(II)](structure.png)
Fig. 71. Structure of Platinum(II) xanthate complexes

The compounds (I), (II), and (III) (Fig. 71) have been found to exceed the activity of cisplatin and in addition are more active at pH 6.8, conditions found frequently in tumor tissues.

Some non platinum xanthate complexes were also found to possess cytotoxicity on tumor cells. Xanthate residues which were highly effective in platinum complexes were used to synthesize gold, nickel, copper, palladium and rhodium complexes. The palladium complexes (IV), (V) and (VI) were identified as the most active derivatives (Fig. 72).

Fig. 72. Structure of some non Platinum xanthate complexes
These were synthesized by the reaction of corresponding potassium salt of O-alkyldithiocarbonates (K$_2$S$_2$COR) with dipotassium tetrachloropalladate(II), (K$_2$PdCl$_4$). The cyclohexyl gold derivative displayed some activity (Fig. 73).

![Structure of Gold(I) xanthate](image)

**Fig. 73. Structure of Gold(I) xanthate**

Bismuth and rhodium derivatives of ethyl, isopropyl, and cyclohexyl complexes show significant cytotoxic activity (Fig. 74).

![Structure of xanthate complexes of Bismuth and Rhodium](image)

R = ethyl, isopropyl, cyclohexyl

**Fig. 74. Structure of xanthate complexes of Bismuth and Rhodium**

All Nickel derivatives displayed intermediate activity while copper ethyl derivatives had only low activity.

The xanthate tricyclodecan-9-yl-xanthogenate (D609) (Fig. 75) displays antiviral, antitumoral properties that are inversely proportional in vitro to the serum concentration. Accordingly, it has been found that D609 in combination with undecanoic acid, has a synergistic antiviral activity$^{251}$. 

![Structure of xanthate complexes of Bismuth and Rhodium](image)
Xanthates form hydrophobic complexes with heavy metals and may therefore facilitate the uptake of metals from water by fish. In presence of complexants, the toxicity of heavy metals and their uptake by aquatic animals can be reduced. 3 x 10^-7 M isopropyl xanthate increases the accumulation of lead in trout *Salmo trutta*. This increase was ascribed to the formation of a non polar lead xanthate complex that was assumed to facilitate the penetration of gill by the metal^{252-254}. The above observations suggest that at high concentrations, xanthates can increase the biological availability of metals to aquatic animals. These xanthates are found to increase the cytotoxicological risk posed by heavy metals by binding them in hydrophobic complexes. However concentration of xanthates in the environment are usually not high enough to allow the formation of hydrophobic complexes.

Xanthates find a wide range of applications in analytical chemistry. This group of compounds is frequently utilized for the extraction and quantification of elements by conventional methods. These have been extensively employed as reagents in chemical analysis for the separation and quantitative determination of cations of transition metals by taking advantage of the low solubilities of transition metal xanthates, and for the analysis of alcohols and carbon disulphide by their quantitative conversion to xanthates^{255}.

Potassium ethyl and benzyl xanthates are well utilized reagents in conventional as well as radiochemical methods for the extraction and quantification of number of metals. The substoichiometric radiochemical extraction of cobalt with potassium ethyl and benzyl xanthates was previously reported^{256-258}. The other xanthates were not yet used for radiochemical determination of cobalt.

A rapid and sensitive sub stoichiometric radiochemical procedure had been developed for the extraction of cobalt with potassium salts of ethyl, propyl, butyl, pentyl and benzyl xanthates. The relative extractabilities of the cobalt-xanthate complexes into chloroform and carbon tetrachloride were studied. Substoichiometric quantification methods were developed in each case and...
utilized to determine the cobalt content present in standard solutions as well as biological samples\textsuperscript{259,260}.

Xanthates have been shown to inactivate the Phenobarbital inducible rat cytochrome P450 2B1 as well as its human homologue P450 2B6. The loss in enzymatic activity was due to covalent binding of a reactive xanthate intermediate to the P450 2B1 apoprotein. Long chain xanthates were able to affect the rate of the first electron transfer in the P450 catalytic cycle by stabilizing the heme in its low spin state. Also, n-octylxanthate metabolism leads to very little observable oxy-ferro intermediate complex formation. Thus covalent modification of P450 2B1 by reactive intermediate of xanthates reduces the rate of electron transfer\textsuperscript{261,262}.

Certain xanthates when complexed with some antibiotics are found to control their activity. Cellulose xanthate-metal-tetracycline complexes (MCX-metal-Tc) were prepared and evaluated as a controlled release system for the antibiotics. Microcrystallized cellulose was chemically modified to cellulose xanthate (MCX). Furthermore, MCX-metal-Tc manifested antibacterial activity that lasted for 7-22 days. These results suggest that MCX-metal-Tc is a Polymeric antibacterial agent with prolonged antibacterial activity.

Xanthates are thus considered to be the promising biological and industrial reagents.