

Chapter-I

General introduction

An Overview of coordination chemistry

Historically, inorganic chemistry is the oldest branch of chemistry. Classical inorganic chemistry was primarily concerned with the preparation and studies of the properties of all the elements and their compounds, including the simple compounds of carbon.

It is very difficult to determine the exact date of preparation of the first coordination compound. The chemistry of complexes may be said to have originated in 1704 with the discovery of Prussian blue by Diesbach, a colour maker. After this one might cite the investigation of the products of oxidation of ammonical cobalt solution of Tassaert (1799). In the years that followed, Cleve, Wolcott Gibbs, Blomstrand and Fermy did a large amount of effort towards the study of complexes.

By 1870, a great deal of information on the complexes had been gathered and it was Prof. Jorgenson who for the first time methodized much of this field by the preparation and characterization of a large number of complex compounds.

An understanding of coordination compounds and their properties began with the work of Alfred Werner. In 1893, Werner proposed an interpretation of coordination compounds which emphasized the number and nature of the groups attached to the metal ion. Werner's theory represent a quantum jump in the history of coordination chemistry, and the most of the 20th century contributions to coordination chemistry has been developments, extensions or confirmation of Werner's theory rather than ideas incompatible with, or opposed to it. Since its promulgation and general acceptance over the decades between 1890 and 1910, it has provided a central trunk from which many fruitful branches of transition chemistry have grown and flourished¹.

His theory replaced the older concepts of Berzelius (1819), Grohen (1837), Claus (1856), Blomstrand (1869) and Jorgenson (1894) and became a fundamental part of the electronic theory of valency formulated by G.N.Lewis (1916) and applied extensively to coordination compounds by N.V.Sidgwick (1927).

Revival of classical crystal field theory (Bethe, 1929) and its further sophistication in to the ligand field theory by Orgel, Jorgenson, Ballhausen and others during the 1950s to early 1960s is another significant advancement which could provide quantitative interpretations of the features of spectra and several other properties of transition metal compounds that was hardly possible on the basis of the valence bond concept of Pauling (1931) despite initial success of Pauling's view to explain in general the stereochemistry and gross magnetic behaviour of transition metal compounds.

One may immediately ask why this group of compounds should be singled out for special study. There are several answers to such a question but some of these are outlined below:

- a) These compounds are formed by large number of elements.
- b) Their applications more numerous than might be expected and many new applications are being discovered.
- c) Many chemical phenomena are exhibited to a superlative degree by these compounds (i.e., molecular rotation of polarized light)

The growth of the coordination chemistry has been three dimensional, encompassing breadth, depth and applications. The ongoing respect for the evolving science is apparent in the five Nobel prizes that have been impinged heavily on the subject (A. Werner, 1913; M.Eigen, 1967, Wilkinson and Fischer, 1973; H.Taube, 1983; Cram, Lehn and Pederson, 1987). The first (Werner) and last (Cram, Lehn and Pederson) in the list recognized the old and the new realms of coordination chemistry specifically².

The steady improvement in synthetic methodology allows us to foresee coordination chemistry entering a phase of relative rather than investigative chemistry. The development of complexes for application in medicine is an obvious

example. The use of metal complexes in therapy and diagnostic imaging is increasing. Throughout history, both ancient and modern, metal compounds have been used in medicine to treat a variety of ailments and a remarkable example being cis-platin, cis-PtCl₂(NH₃)₂, introduced by Rosenberg³. This discovery led to a veritable avalanche of research in platinum chemistry and for a continuing search for the most effective anticancer drug⁴⁻⁶.

The chelation plays a definite role in the cause and treatment of a cancer is a significant development of the 1960s⁷.

A triplatinum complex (**Fig-1**) was shown to be cytotoxic at nanomolar levels for several different concentrations allowing for the potential to dose at much lower concentrations than cisplatin. It has also shown potential in treating gl malignancies which have been otherwise untreatable using cisplatin. This compound is licensed to Novus pharma and is currently undergoing phase II clinical trial for the treatment of several different cancers⁸.

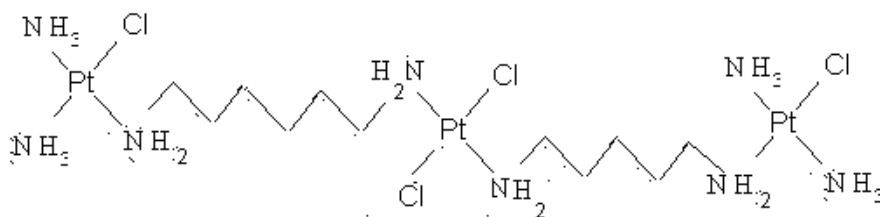


Fig-1

Gold compounds like Aurofin, (2,3,4,6-tetra-o-acetyl-1-thio-β-D-glucopyranoside-5) triethyl phosphine gold(I)^{9,10} are applied as oral drugs against rheumatoid arthritis^{10,11}.

Coordination chemistry has its greatest application in the field of hydrometallurgy and pyrometallurgical operations. Use of carboxylic acid extractant to recover nickel and cobalt¹² and for removal of iron (III) from solution of rare earth metals¹³ has been reported. Versatic acid has been used for the production of pure Eu (III), La (III), Yb (III) oxide¹³ and to recover indium and gallium from solutions obtained from leaching of bauxites, zinc minerals and coal ash¹⁴. Solvent extraction of

copper and nickel by ortho hydroxyl oximes is used widely throughout the world.

Many metal complexes find applications in the field of catalysis.² Among the top performers in this class (and the elements involved) are the Wilkinson catalyst for the hydroformylation reaction (Rh), the conversion of ethylene to acetaldehyde (Pd) and olefin polymerization (Zr, Ni); there are many others too numerous to mention. It should also be noted that one of the greatest recent advances in organic chemistry, is asymmetric synthesis, depends entirely upon transitional metal atoms as the catalytic centres.

The ever increasing applications of metal complexes in various fields of science are the driving force for the research and development of coordination chemistry. In present study the coordination chemistry of ruthenium was studied.

Discovery

Ruthenium-the atomic number is 44 and the chemical symbol is Ru. The name derives from the Latin Ruthenia for the “old name of Russia”. Ruthenium was discovered by J.A.Sniadecki (vilno, Poland) in 1808, but not recognized as an element. It was discovered in a crude platinum ore by the Russian chemist Gottfried Wilhelm Osann in 1828. Osann thought that he had found three new metals in the sample, pluranium, ruthenium and polinium. He later withdrew his claim of discovery. In 1844 the Russian chemist Karl Karlovich Klaus was able to show that Osann’s mistake was due to the impurity of the sample but Klaus was able to isolate the ruthenium metal from the impure oxide and he retained Osann’s original name of ruthenium.

Appearance

Ruthenium is a hard lustrous white metal that does not tarnish at room temperature.

Source

Ruthenium is found as the free metal but also associated with other platinum metals in the mineral pentlandite found in the USA, and pyroxinite, found in South Africa. Commercially it is obtained from the wastes of nickel refining.

Uses

Ruthenium is one of the most effective hardeners for platinum and palladium and is alloyed with these metals to make electrical contacts for severe water resistance. It is also a versatile catalyst, used to split hydrogen sulphide for example.

General information

Ruthenium is unaffected by air, water and acids but reacts with alkali and is attacked by halogens.

Physical information

Atomic number	44
Ground state electronic configuration	[Kr] 4d ⁷ 5s ¹
Oxidation states	+2,+3,+4,+5,+6,+7,+8
Relative atomic mass (¹² C=12.000)	101.07
Melting point/K	2583
Boiling point/K	4173
Density/kg m ⁻³	12370 (293K)
Electron affinity (M-M)/kJ mol ⁻¹	-148
Enthalpy of Fusion/kj mol ⁻¹	23.7
Enthalpy of Vapourisation/kj mol ⁻¹	587

General remarks: Stereochemistry

The chemistry of ruthenium bears little resemblance to that of iron except in compounds such as sulphides or phosphides and in complexes with ligands such as CO, PR₃ or *h*⁵-C₅H₅. The higher oxidation states, VI and VII are much more readily obtained than for iron and there is an extensive and important chemistry of the tetroxides, MO₄, oxohalides and oxo anions.

The principal lower oxidation states for ruthenium are 0, II and III. There is no evidence for the (I) oxidation state although some brown air sensitive solutions obtained by reduction of RuCl₃ in dimethylacetamide by hydrogen may contain a Ru^I species¹⁵. The oxidation states and stereochemistries are summarized in

Table-1.

Table-1*Oxidation States and Stereochemistry of Ruthenium*

Oxidation state	Coord No	Geometry	Examples
Ru ^{-II}	4	Tetrahedral ?	Ru(CO) ₄ ²⁻ , Ru(diphos) ₂ ²⁻
Ru ⁰ , <i>d</i> ⁸	5	tbp ?	Ru(CO) ₅ , Ru(CO) ₃ (PPh ₃) ₂
Ru ^I , <i>d</i> ⁷	6 ^c		[<i>h</i> ⁵ -C ₅ H ₅ Ru(CO) ₂] ₂
Ru ^{II} , <i>d</i> ⁶	5		Ru(Cl) ₂ (PPh ₃) ₃
	5	tbp	RuHCl(PPh ₃) ₃
	6 ^a	Octahedral	[RuNOCl ₅] ²⁻ , Ru(bipy) ₃ ²⁺ [Ru(NH ₃) ₆] ²⁺
Ru ^{III} , <i>d</i> ⁵	6 ^a	Octahedral	[Ru(NH ₃) ₅ Cl] ²⁺ , [RuCl ₅ H ₂ O] ²⁻ , K ₃ [Ru F ₆]
Ru ^{IV} , <i>d</i> ⁴	6 ^a	Octahedral	K ₂ [Ru Cl ₆], RuO ₂ ^b
Ru ^V , <i>d</i> ³	6	Octahedral	K[Ru F ₆], [Ru F ₅] ₄
Ru ^{VI} , <i>d</i> ²	4	Tetrahedral	RuO ₄ ²⁻
	6	Octahedral	Ru F ₆
Ru ^{VII} , <i>d</i> ¹	4	Tetrahedral	RuO ₄ ⁻
Ru ^{VIII} , <i>d</i> ⁰	4	Tetrahedral	RuO ₄
^a Most common states for Ru, ^b Metal-metal bond present, ^c If <i>h</i> ⁵ -C ₅ H ₅ assumed to occupy three coordination sites			

The 0 state, *d*⁸.

The chemistry in this state is primarily metal carbonyls; mononuclear and poly nuclear carbonyls.

The II state, *d*⁶.

Complexes with CO, PR₃ and similar *II* acid ligands are exist. A large number of complexes exist with ligands such as Chloro, ammine etc. All Ru^{II} complexes are octahedral and diamagnetic as expected for the t_{2g}⁶ configuration.

The III state, d^5 .

There is an extensive chemistry with π acid and σ - donor ligands. All the complexes are low spin type with one unpaired electron and are octahedral.

Ruthenium (III) chloro complexes.

These are among the best characterized complexes. When RuO_4 is collected in concentrated HCl and the solution is evaporated, a dark red, deliquescent, crystalline material is obtained. This commercial product is usually called " $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$," is the starting point for the preparation of most ruthenium compounds. It is readily soluble in water, ethanol, acetone and similar solvents. Only with very concentrations of Cl^- is $[\text{RuCl}_6]^{3-}$ formed. the rate of replacement of Cl^- by H_2O increases with the number of Cl^- ions present, so that while the aquation of $[\text{RuCl}_6]^{3-}$ to $[\text{RuCl}_5(\text{H}_2\text{O})]^{2-}$ is of the order of seconds in water, the half reaction time for conversion of $[\text{RuCl}(\text{H}_2\text{O})_5]^{2+}$ into $[\text{Ru}(\text{H}_2\text{O})_6]^{3+}$ is about a year. The yellow trans- $[\text{RuCl}_2(\text{H}_2\text{O})_4]^+$ and green trans- $[\text{RuCl}_4(\text{H}_2\text{O})_2]^-$ are best obtained by oxidation of $[\text{Ru}_5\text{Cl}_{12}]^{2-}$. Ruthenium (III) chloro species catalyze the reduction of Fe^{+3} by H_2O and also the hydration of acetylenes.

The IV state, d^4 .

In this state most complexes are neutral or anionic. All the complexes have octahedral or distorted octahedral structures. Ru (IV) complexes have practically normal magnetic moments at room temperature (2.7-2.9 BM), but these also decrease with $T^{1/2}$ as the temperature is lowered. Little is known of the d-d transitions since the relevant absorption bands are severely masked by strong charge transfer bands.

Applications of Ruthenium compounds

Ruthenium compounds in general are well-suited for medicinal applications¹⁶. They have been investigated as immunosuppressants^{17,18}, nitric oxide scavengers¹⁹, antimicrobial agents²⁰ and antimalerials²¹. Ruthenium red is known to inhibit calcium ion uptake by mitochondria²². Many groups are working on platinum based antitumor drugs since the discovery of the tumor-inhibiting qualities of Cisplatin by Barnett Rosenberg in 1969, a conclusive mode of action has not been found as yet. Early

interest in the anticancer activity of ruthenium complexes stemmed from the observations of Clarke that Ru(III) amines, e.g. $[\text{RuCl}_3(\text{NH}_3)_3]$, are active anticancer agents²³. However these were too insoluble for clinical use. Imidazolium trans-imidazoledimethyl Sulfoxide tetrachloro ruthenate (NAMI-A), which is one of the best leading ruthenium complexes with the best chances of becoming an anticancer drug²⁴. Several analogues of NAMI-A are synthesized and evaluated as cytostatic agents²⁵.

$[\text{Ru Cl}_2 (\text{DMSO})_2\text{L}]$ (L= α -5-nitrofuryl semicarbazone derivative) were excellent DNA binding agents for Calf thymus DNA, but were found to be non cytotoxic on a range of tumour cell lines²⁶.

Many metal complexes find applications in the field of catalysis. Wilkinson and coworkers have shown that the complex $[\text{RuCl}_2(\text{PPh}_3)_3]$ and complexes derived from it can be used for the preferential hydrogenation of terminal double bonds²⁷.

In the present day scenario with a gloomy future there is considerable interest for the production of H_2 for use as a fuel by water splitting in a photochemical process in presence of metal compounds or complexes as catalysts. A few such systems have been reported and further work to achieve greater efficiency for practical use is much of promise. The most effective systems reported so far based on $\text{Ru}(\text{bipy})_3^{2+}$ type complexes as photo catalysts²⁸.

Nanomaterials, the materials of the 21st century, are under close scrutiny both for fundamental and technological applications such as for instance microelectronics, chemical, gas and biosensors as well as novel catalytic and photovoltaic devices. Ruthenium dioxide is a well-known metallic oxide used as resistors, electrochemical capacitors as well as catalysts. However, the high effective cost of the ruthenium devices has contributed to a decrease in its material research activity^{29,30}.

Considerable attention has recently been focused on ruthenium and ruthenium containing films for a variety of semiconductor applications. Specifically, ruthenium is a candidate material for metal electrodes in DRAM applications and ruthenium and/or ruthenium/ tantalum alloys are candidate materials for gate electrodes in logic applications. Ruthenocene and 1,1'-diethylruthenocene have been described in the

literature as promising ALD and CVD precursor candidates for this application. A report detailing the use of 1-propylruthenocene as a precursor for the deposition of thin films of Ru has also recently appeared. The generation of other functionalized ruthenocenes may result in precursors with superior characteristics that are capable of taking advantage of the knowledge that has been gathered surrounding the optimization of deposition conditions for ruthenocene^{31,32}.

2,6-Diformyl-*p*-cresol as binucleating precursor

Since the report by Robson³³⁻³⁶ in 1970 of a binucleating Schiff base ligands obtained by condensation of 2,6-diformyl-*p*-cresol with 2-aminophenol, many example of similar compartmental ligands have been reported³⁷. the binucleating ability of these ligands stems from the readiness of the phenol to deprotonated and bridge two metal ions³⁸⁻⁴⁰. Recently trinuclear and tetra nuclear complexes with ligand derived from the condensation of 2,6-diformyl-*p*-cresol and selected diamines, hydroxyl amine have been reported. In our laboratory dinuclear and tetranuclear complexes derived from the condensation of 2,6-diformyl-*p*-cresol and selected diamines, namely, thiosemicarbazide, carbohydrazide, thiocarbohydrazide, substituted 1,2,4 triazoles, hydrazides⁴¹⁻⁴⁶ have been reported.

Binucleating ligands are also helpful in providing the behaviour for the synthesis of structural and functional models of metalloenzymes having homodinuclear center at the active sites. Compartmental macrocyclic ligands having two phenolic oxygens as an endogeneous bridge have been developed for this purpose, because they bind two metal centers in close proximity relevant to the active sites of bimetallic enzymes. Recently X-ray crystallographic studies have indicated that most bimetallic biosites are asymmetric with respect to the donor atoms about the metal centres, the nature of the metal ions, the coordination number and the geometric arrangement of the donor atoms⁴⁷⁻⁵¹.

3-Acetyl coumarin

In the year 1868 Perkin first prepared coumarin, which is now known as the classical synthetic method bearing his name⁵². Earlier coumarin was isolated by Vogel⁵³ in 1820 from Tonka beans. The seeds contain a fragrant phenolic compound

coumarin, which is used in perfumes and as vanilla like favouring agent in ice creams, candy and pipe tobaccos. Coumarin has been shown to be carcinogenic when burnt. Coumarin is also an anticoagulant that represses the synthesis of the protein prothrombin in the presence of vitamin K.

The biologic importance of coumarin derivatives has anticoagulant as aflatoxins, myotoxins and antibiotics have led to a considerable amount of synthetic work in the field of coumarin for their pharmacological evaluation. A brief account of some of the importance coumarin derivatives are as follows:

Ron and Mayers⁵⁴ observed its toxic action on algae and found that the present coumarin prevented the growth of *Chlorella vulgaris* in $1.4 \times 10^3 \text{ mol}^{-1}$ concentration. Coumarin inhibits the germination growth of certain roots of the plants. Its effect on wheat, potato is well known and has been reviewed⁵⁵⁻⁵⁶.

Russian workers during their study on the effect of coumarin in higher plants have found that it has growth stimulatory action at lower concentration, and has got a wide range of effects in animals also, such as the depression of smooth muscles and dilation of peripheral blood vessel in frogs, rabbits and mice which were noticed by Rai⁵⁷.

The nature of coordination compounds depends on the metal ion, the donor atom, the core structure of the ligand and the metal ligand interactions⁵⁸. Generally, a metal ion does not form bonds of equal strength with two different donor atoms and a given donor atom does not form bonds of equal strength with different metal ions.

AIM OF OUR RESEARCH

The present thesis entitled “Synthesis and Characterization of Coordination Compounds of Ruthenium” involves synthesis and characterization of some ruthenium complexes with various thiosemicarbazones, Schiff base and thiocarbohydrazones derived from 2,6-diformyl-*p*-cresol and 3-acetylcoumarin moieties. The characterization of these complexes have been carried out on the basis of elemental analysis, room temperature magnetic moment, molar conductance

measurements, thermal analysis, infra red, electronic, electron spin resonance and cyclic voltammetric methods.

From literature it has been observed that the thiosemicarbazones derived from 2,6-diformyl-*p*-cresol are act as a potential pentadentate system with two carbonyl sulphur, two azomethine nitrogens and phenolic oxygen capable of coordination to the metal atom. However it has found to show compartmental behaviour, coordinating to two metal atoms with the phenolic oxygen acting as a bridge between two metal atoms.

The new thiosemicarbazone ligands derived from 3-acetylcoumarin moiety are act as a potential monobasic tridentate manner coordinating to metal via sulphur atom, azomethine nitrogen and lactone carbonyl oxygen.

The new Schiff base ligands derived from 2,6-diformyl-*p*-cresol were act as a potential pentadentate system with NNONN or ONONO coordinating sites.

The new Schiff base ligands derived from 3-acetylcoumarin were act as a potential monobasic tridentate system with O,N,N- or O,N,O- coordinating sites.

The thiocarbohydrazones ligands act as potential bidentate, tetradentate or pentadentate manner.

From literature survey it is clear that no work on ruthenium complexes with above mentioned ligands have been reported. Thus a keen interest o know more about the behaviour of ruthenium and its complexing ability, also to know the mode of coordination of these thiosemicarbazones, Schiff base and thiocarbohydrazones this work has been undertaken.

For convenience the thesis is divided in to six chapters.

Chapter-I: General Introduction.. Presents a brief account of coordination chemistry, chemical behaviour of Ruthenium and aim of the present investigation.

Chapter-II: Compartmental binuclear ruthenium (III) complexes of thiosemicarbazones, gives the details of synthesis of thiosemicarbazone ligands derived from 2,6-diformyl-*p*-cresol and the corresponding ruthenium (III) complexes using these ligands.

Chapter-III: Synthesis and characterization of ruthenium (III) complexes of thiosemicarbazones, deals with the synthesis of thiosemicarbazone ligands derived from 3-acetylcoumarin and the corresponding ruthenium (III) complexes using these ligands.

Chapter-IV: Schiff base compartmental binuclear ruthenium (III) complexes, deals with the synthesis of some selected Schiff base compartmental ligand metal complexes which are derived from the ligands like 2-hydrazino benzothiazole, 4-amino-3-antipyrine, 2-hydroxy-3-hydrazinoquinoxiline, carbohydrazide and semicarbazide as the side arms of 2,6-diformyl-*p*-cresol and the corresponding ruthenium (III) complexes using these ligands.

Chapter-V: 3-Acetyl coumarin Schiff base complexes of ruthenium (III), deals with the synthesis of some selected Schiff base metal complexes which are derived from the ligands like 2-hydrazino benzothiazole, 4-amino-3-antipyrine, 2-hydroxy-3-hydrazinoquinoxiline, carbohydrazide and semicarbazide as the side arms of 3-acetylcoumarin and the corresponding ruthenium (III) complexes using these ligands.

Chapter-VI: Complexes of ruthenium (III) chloride withthiocarbohydrazones, deals with the synthesis of some thiocarbohydrazone ligands derived from 3-acetylcoumarin, salicylaldehyde, substituted salicylaldehyde, 2-hydroxy naphthaldehyde and 2,6-diformyl-*p*-cresol and the corresponding ruthenium (III) complexes using these ligands.

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