# Advanced Transition Metal Chemistry – Periodic Table
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## Lecture – 8
## Coordination Theory

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History of coordination compounds

- The earliest known coordination compound is the bright red alizarin dye first used in **India** and known to the ancient Persians and Egyptians.
- It is a calcium aluminum chelate complex of hydroxyanthraquinone.
- The first scientifically recorded coordination compound was made by German chemist, physician, and alchemist **Andreas Libavius**. He described in 1597 a blue color compound ($[Cu(NH_3)_4]^{2+}$) formed when lime water containing sal ammoniac ($NH_4Cl$) was contacted with brass.

Hello everyone, welcome you all once again to MSB lecture series on advanced transition metal chemistry. Today I shall start discussion on very interesting and important aspect of transition metal chemistry that is coordination theory. Before I proceed further, let me tell you about the history behind this coordination theory. The earliest known coordination compound is the “red alizarin dye” first used in India and also it was known to ancient Persian and Egyptians. It is a calcium aluminum chelate complex of hydroxyanthraquinone.

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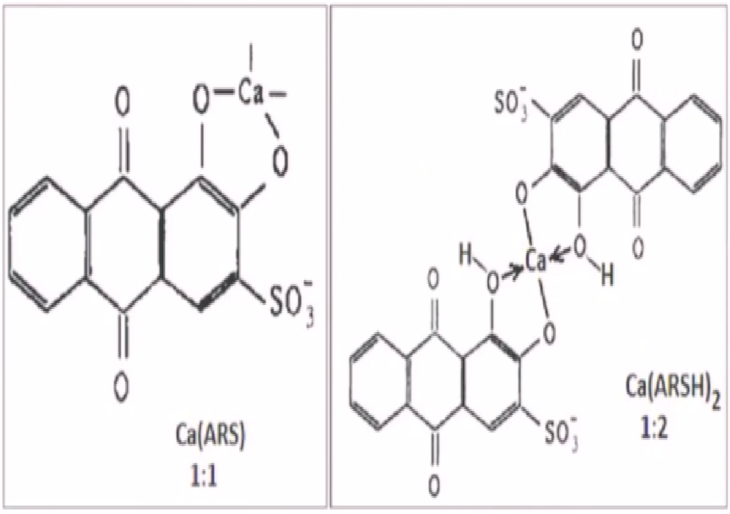

This is how it looks like. The first scientifically recorded coordination compound was made by a `German chemist, physicist and alchemist. Those days every chemist or a physicist or a mathematician used to be alchemist and they used to touch upon all the science subjects. So, among them this German chemist Andreas Libavius was the first one who recorded scientifically inorganic complex for the first time.

What he did was he described in 1597, a blue colour compound having composition of 4 ammonia and a copper 2+ ion. Of course, now, it is known as tetra ammonium copper, formed when lime water containing sal ammoniac; so, those days ammonium chloride was mentioned as sal ammonia. When it was contacted with brass, they observed the formation of this blue colour, that is essentially due to the formation of this compound here. This is the first recorded copper complex or coordination complex.

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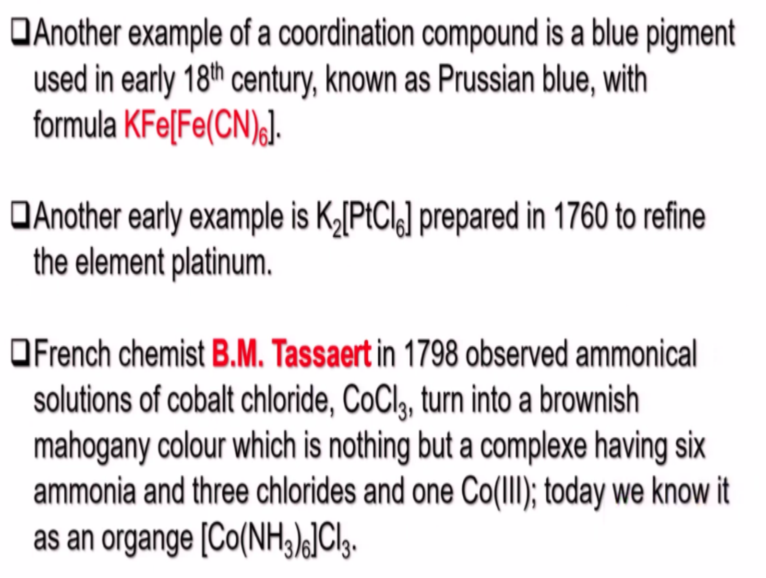

❑ Another example of a coordination compound is a blue pigment used in early 18th century, known as Prussian blue, with formula $KFe[Fe(CN)_6]$.

❑ Another early example is $K_2[PtCl_6]$ prepared in 1760 to refine the element platinum.

❑ French chemist **B.M. Tassaert** in 1798 observed ammonical solutions of cobalt chloride, $CoCl_3$, turn into a brownish mahogany colour which is nothing but a complexe having six ammonia and three chlorides and one Co(III); today we know it as an organge $[Co(NH_3)_6]Cl_3$.

Another example after coordination compound is a well-known blue pigment used in early 18th century known as Prussian blue with formula as shown here $KFeFe(CN)_6$ and in fact has an interesting structure, I shall show you at later stage. Another early example of a coordination complex was potassium hexachloroplatinate that was prepared in 1760 to refine the element platinum.

French chemist B. M. Tassaert in 1798 observed ammonical solution of cobalt chloride turned into a brownish mahogany colour which is nothing but a complex having six ammonia and three chlorides; today we know that it is the hexamine cobalt three chloride, $[Co(NH_3)_6]Cl_3$, so cobalt in +3 state. So, this is the first complex, I would say, with cobalt prepared by B.M. Tassaert in 1798.

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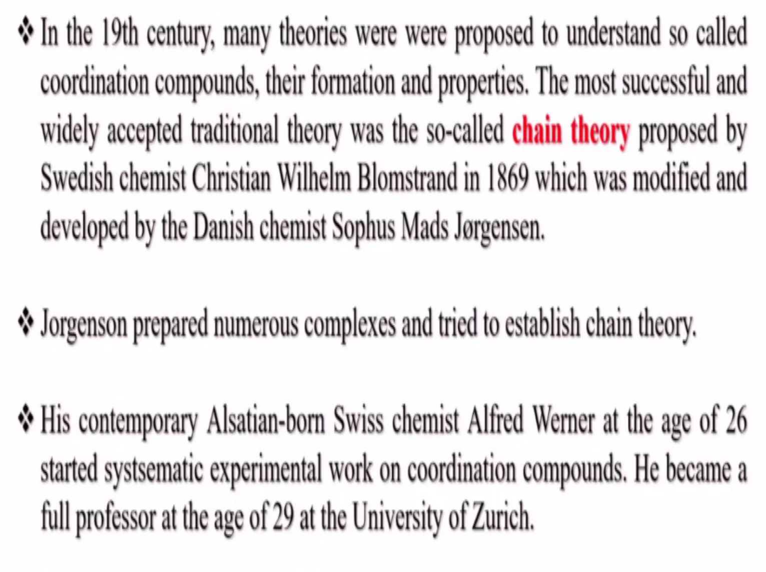

❖ In the 19th century, many theories were were proposed to understand so called coordination compounds, their formation and properties. The most successful and widely accepted traditional theory was the so-called **chain theory** proposed by Swedish chemist Christian Wilhelm Blomstrand in 1869 which was modified and developed by the Danish chemist Sophus Mads Jørgensen.

❖ Jorgenson prepared numerous complexes and tried to establish chain theory.

❖ His contemporary Alsatian-born Swiss chemist Alfred Werner at the age of 26 started systsematic experimental work on coordination compounds. He became a full professor at the age of 29 at the University of Zurich.

In the 19th century that means during the period when Mendeleev proposed periodic table many theories were proposed to understand the so called coordination compounds, and their formation and properties. The most successful and widely accepted traditional theory that time was, so called, chain theory proposed by a Swedish chemist, Blomstrand in 1869 which was modified and developed by Danish chemist Sophus Mads Jorgensen.

In fact, Blomstrand and Jorgensen were contemporaries of Alfred Werner, who proposed coordination theory after studying it very systematically. In fact, it is very interesting to know about the rivalry between Jorgensen and Alfred Werner. So, Jorgensen prepared numerous complexes and tried to establish his chain theory to explain the formation, properties and reactivity of coordination compounds.

As I said, his contemporary Alsatian-born Swiss chemist Albert Werner, at the age of 26, he started systematic experimental work on coordination compounds. So, he became a full professor at the age of 29 at the University of Zurich. In fact, I would say he is the most sophisticated inorganic chemist of that time, when Jorgensen and Blomstrand were proposing coordination theory and try to make it universal.

He started in an unconventional way working very systematically giving more importance to quantitative analysis rather than qualitatively looking into something and putting their hypothesis. In fact, the critical evaluation of Werner’s theory by Jorgensen and his group made him refine and refine and eventually come up with an excellent hypothesis to explain almost all properties of coordination compounds including their preparation, structure and all those things.

And during that time without having much support from analytical instruments and spectroscopic instruments, he did a remarkable job and he proposed very interestingly octahedral geometry, square planar geometry, tetrahedral geometry and also he brought concept of primary valency, secondary valency and all those things and before we proceed further, I will try to tell you what is the so called chain theory proposed by Blomstrand and Jorgensen.

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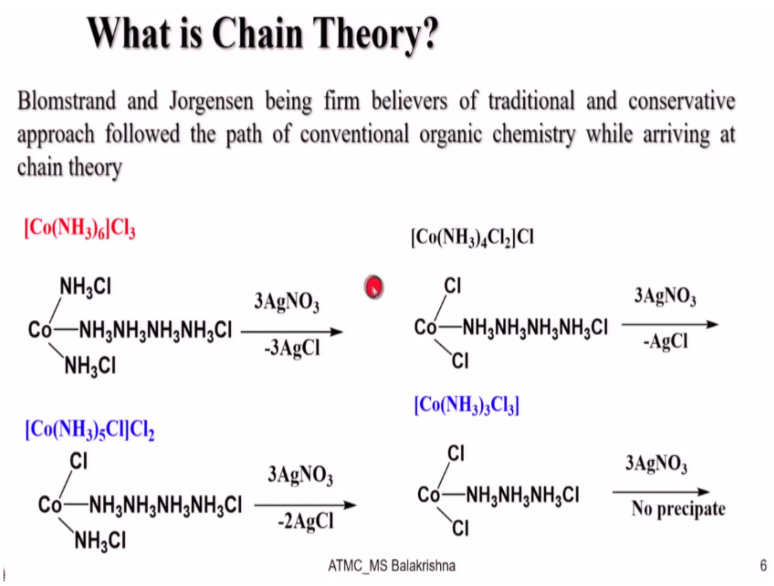

## What is Chain Theory?

Blomstrand and Jorgensen being firm believers of traditional and conservative approach followed the path of conventional organic chemistry while arriving at chain theory

$[Co(NH_3)_6]Cl_3$

$[Co(NH_3)_4Cl_2]Cl$

$[Co(NH_3)_5Cl]Cl_2$

$[Co(NH_3)_3Cl_3]$

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And you can see Blomstrand and Jorgensen, actually firm believers of traditional and conservative approach, followed the path of conventional organic chemistry, while arriving at their theory. What the theory says is when they made hexamine cobalt 3 chloride, $[Co(NH_3)_6]Cl_3$, they believed that a transition metal can have a valency of 3, not beyond that one. In order to satisfy valency 3, they wrote this structure for hexamine cobalt 3 chloride.

And then later they reacted this one with silver nitrate and anticipating the precipitation of 3 silver chloride. In fact, as they expected, when this compound having this empirical formula treated with three equivalents of silver nitrate, it led to the precipitation of three equivalents of silver chloride. This kind of structure is based on their understanding of organic chemistry where $CH_2$ groups are linked to each other.

So, that is the reason they call it as chain theory, where instead of writing now well-known octahedral geometry they wrote in this fashion showing chloride outside and also putting a chain of 4 ammonium molecules and chlorine at the end and they proposed that since these chlorides are far away from cobalt, the precipitation of these things or elimination of these things as silver chloride would be rather easy.

So, then they extended to this compound here. In this compound also keeping the same convention, they wrote like this, showing one covalent bond here and another ammonia and putting chloride on ammonia and they satisfied the coordination number we call it as 5 here. And in this case, they were succeeded precipitating two chlorides and they concluded that yes since this is very close to cobalt, so it cannot be precipitated out.

And if it is far, any chloride atom that is far from cobalt binding in this fashion, then can give, the outer chlorides can come out as silver chloride. So, in this case they got two chlorides coming out, again their hypothesis was looking convincing. And then when they went for this one. Again, they wrote this structure here and to their surprise, so when they treated with excess of silver nitrate, they could get only one silver precipitating out, again proving their chain theory.

In this case, they failed here. So when they had three ammonia and three chloride and it is a neutral complex, it is not ionic, no chlorides are there in the outer sphere. So, in this case, they expected at least one silver chloride precipitation, so that did not happen. So, when they treated with silver nitrate, there was no precipitation of silver chloride. So, this chain theory miserably failed. But still they were proposing and arguing and criticizing systematic work carried out by Werner.

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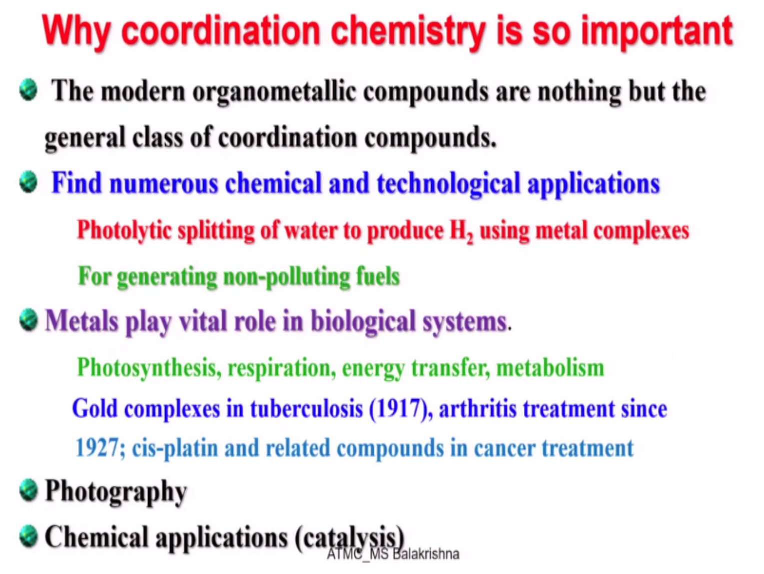

Why coordination chemistry is so important

- The modern organometallic compounds are nothing but the general class of coordination compounds.
- Find numerous chemical and technological applications
  Photolytic splitting of water to produce $H_2$ using metal complexes
  For generating non-polluting fuels
- Metals play vital role in biological systems.
  Photosynthesis, respiration, energy transfer, metabolism
  Gold complexes in tuberculosis (1917), arthritis treatment since 1927; cis-platin and related compounds in cancer treatment
- Photography
- Chemical applications (catalysis)

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Before I proceed, I have to tell you about the painstaking work of Werner's research and work on coordination compounds. Let me tell you why coordination chemistry is so important today. The modern organometallic compounds are nothing but the general class of coordination components, and they find numerous chemical and technological applications.

For example, if you want to split water photolytically to produce $H_2$ keeping renewable energy in mind, you have to go for metal complexes and also for generating non-polluting fuels. And we all know that metals play a vital role in biological systems. We talk about metalloenzymes, in fact enzymes observed in plants as well as living beings have no identity if their metal present in their system is taken out.

So, that indicates the importance of metals in biological systems. You consider photosynthesis, respiration, energy transfer, metabolism every biological process involves a metalloenzyme that shows the importance of metals in biology and also most of the metals look like a metal complex. And of course, gold complex was used for tuberculosis treatment as early as 1917 and in arthritis treatment also gold compounds were used.

And 1927 onwards cisplatin and related compounds are used in cancer treatment, chemotherapy and even now cisplatin is used for prostate cancer and several platinum derivatives are used in various cancer treatment. And photography, of course now we have digital photography. When analog photography was there, the greatest contribution of coordination compounds was in photography.

And of course, chemical application in catalysis is well known, both coordination compounds and organometallic components play a major role in homogeneous catalysis, to an extent also in heterogeneous catalysis.

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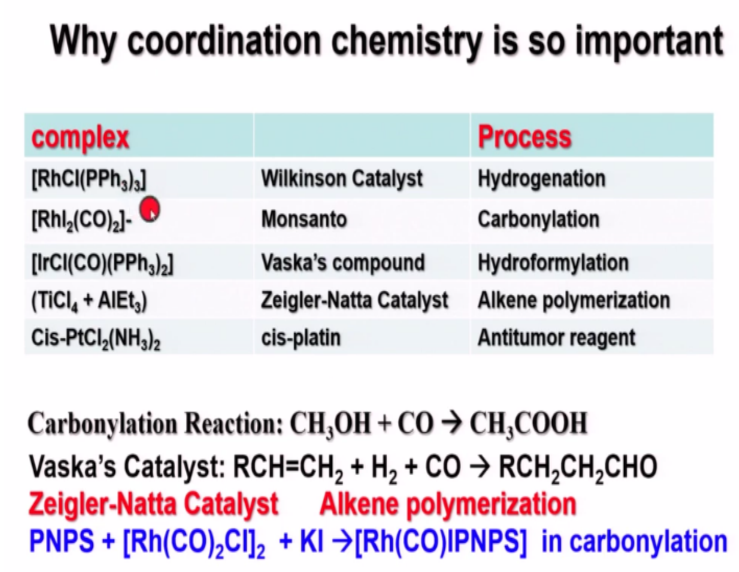

## Why coordination chemistry is so important

| complex | | Process |
|---|---|---|
| $[RhCl(PPh_3)_3]$ | Wilkinson Catalyst | Hydrogenation |
| $[RhI_2(CO)_2]-$ | Monsanto | Carbonylation |
| $[IrCl(CO)(PPh_3)_2]$ | Vaska's compound | Hydroformylation |
| $(TiCl_4 + AlEt_3)$ | Zeigler-Natta Catalyst | Alkene polymerization |
| Cis-$PtCl_2(NH_3)_2$ | cis-platin | Antitumor reagent |

Carbonylation Reaction: $CH_3OH + CO \rightarrow CH_3COOH$

Vaska's Catalyst: $RCH=CH_2 + H_2 + CO \rightarrow RCH_2CH_2CHO$

Zeigler-Natta Catalyst Alkene polymerization

PNPS + $[Rh(CO)_2Cl]_2$ + KI $\rightarrow$ [Rh(CO)IPNPS] in carbonylation

So, here if you see Wilkinson catalyst and this is used in hydrogenation and several other organic transformations and this rhodium iodide compound is used in Monsanto company, they started using in Monsanto company for carbonylation. The carbonylation is nothing but the treatment of methanol with carbon monoxide in which carbon monoxide is inserted to form acetic acid.

And Vaska’s compound: this trans iridium chloro carbonyl bistriphenylphosphine, trans-$[IrCl(CO)(PPh_3)_2]$, compound was used in hydroformylation. This is a typical hydroformylation reaction I have shown here and the combination of titanium tetrachloride and triethyl aluminum was used by Ziegler-Natta in alkene polymerization and the utility of cisplatin in antitumor cancer treatment is well known and in my own research I had developed a phosphorus and sulfur donor compound.

When treated with rhodium-chloro-carbon dimer, it formed chelate compound that shows interesting and almost comparable catalytic activity, the one that was used by Monsanto for carbonylation. So, let us come back to coordination theory; coordination theory and coordination compounds is synonymous with Alfred Werner. As I mentioned, at the age of 29, he became the full professor of chemistry at Zurich University.

And he started this pioneering work at the age of 26 when no instrumental facilities whether it is analytical or spectroscopic was available, not only that, even the atomic structure was not known, and even electrons were not known.

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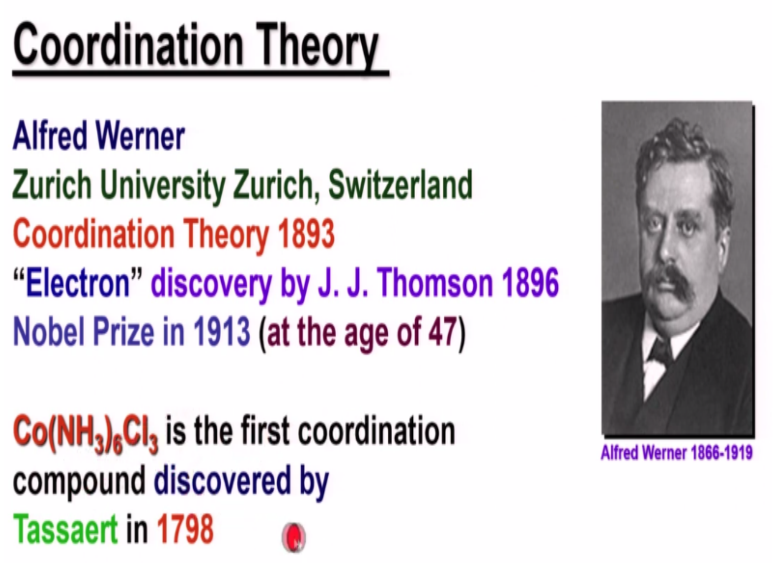

## Coordination Theory

Alfred Werner
Zurich University Zurich, Switzerland
Coordination Theory 1893
“Electron” discovery by J. J. Thomson 1896
Nobel Prize in 1913 (at the age of 47)

$Co(NH_3)_6Cl_3$ is the first coordination compound discovered by Tassaert in 1798

Alfred Werner 1866-1919

He proposed his coordination theory in 1893. You recall electrons were discovered by J J Thompson in 1896 and for his painstaking work he was awarded Nobel Prize in 1913 at the age of 47. And as I mentioned hexamine cobalt 3 chloride is the first coordination compound discovered by Tassaert in 1798.

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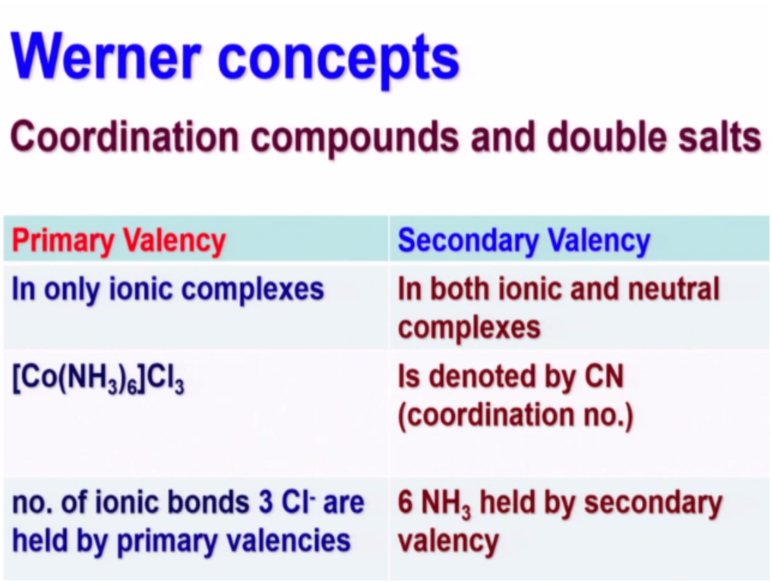

## Werner concepts

### Coordination compounds and double salts

| Primary Valency | Secondary Valency |
|---|---|
| In only ionic complexes | In both ionic and neutral complexes |
| $[Co(NH_3)_6]Cl_3$ | Is denoted by CN (coordination no.) |
| no. of ionic bonds 3 $Cl^-$ are held by primary valencies | 6 $NH_3$ held by secondary valency |

What are the Werner's concepts? So, he clearly distinguished between coordination compounds and double salts. Coordination compounds when you put into aqueous medium, or solution they retain their identity, whereas double salts, they lose their identity and disintegrate into the corresponding ions. So, this is the first attempt he made in establishing coordination theory by distinguishing coordination compounds from double salts.

What is primary valency? In only ionic complexes, you can see primary valency but in secondary valency in both ionic and neutral complexes you can see, that one. For example, if you consider hexamine cobalt chloride and here this ammonia inside is denoted by a coordination number. So, if it is 6, secondary valency 6 or coordination number is 6 and outside whatever is there outside the bracket as counter anions is primary valency.

They are considered as primary valency, and number of ionic bonds are 3. $Cl^-$, they are held by primary valency. That means they are involved in ionic bonding with cobalt, whereas this ammonia inside the coordination sphere are involved in covalent bonding, and they are with ionic bonds. So, 6 ammonia held by secondary valency. So, this is how clearly he brought the term primary valency and secondary valency, and secondary valency is nothing but the coordination number.

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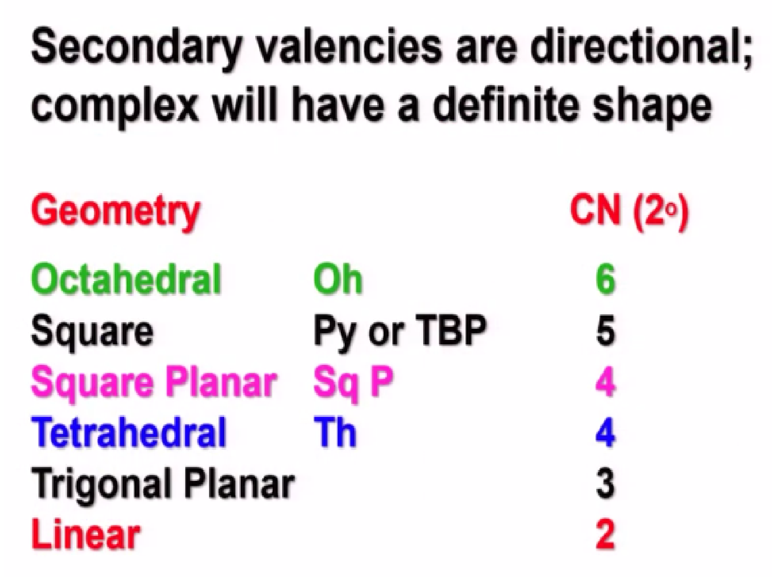

Secondary valencies are directional; complex will have a definite shape

| Geometry | | CN ($2^{o}$) |
|---|---|---|
| Octahedral | Oh | 6 |
| Square | Py or TBP | 5 |
| Square Planar | Sq P | 4 |
| Tetrahedral | Th | 4 |
| Trigonal Planar | | 3 |
| Linear | | 2 |

And based on coordination number he proposed various geometries. For example, when coordination number was 6 without any ambiguity, he proposed octahedral geometry and when coordination number was 5 he could tell about square pyramidal geometry and penta trigonal bipyramidal geometry. So, when the cooordination number 5, he proposed both square pyramidal geometry and trigonal bipyramidal geometry.

And for coordination number 4 he proposed both square planar geometry as well as tetrahedral geometry, depending upon the metal ions, and the type of ligands involved. When coordination number was 3, he proposed trigonal planar and for coordination number 2 he proposed linear geometry. And all these geometry and structural establishment and primary valency, secondary valency all these things he could do efficiently because of his quantitative thought and excellent experimental skills and also using conductivity measurements. Beyond that, he did not have any other aid to support his work.

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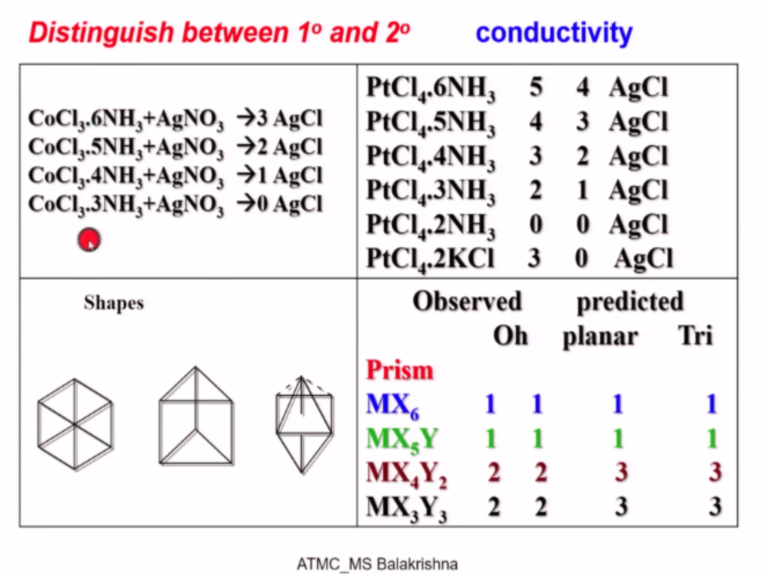

Distinguish between 1° and 2°　　conductivity

$CoCl_3.6NH_3+AgNO_3 \rightarrow 3\ AgCl$
$CoCl_3.5NH_3+AgNO_3 \rightarrow 2\ AgCl$
$CoCl_3.4NH_3+AgNO_3 \rightarrow 1\ AgCl$
$CoCl_3.3NH_3+AgNO_3 \rightarrow 0\ AgCl$

| | | | |
|---|---|---|---|
| $PtCl_4.6NH_3$ | 5 | 4 | AgCl |
| $PtCl_4.5NH_3$ | 4 | 3 | AgCl |
| $PtCl_4.4NH_3$ | 3 | 2 | AgCl |
| $PtCl_4.3NH_3$ | 2 | 1 | AgCl |
| $PtCl_4.2NH_3$ | 0 | 0 | AgCl |
| $PtCl_4.2KCl$ | 3 | 0 | AgCl |

Shapes

| | Observed | | predicted | |
|---|---|---|---|---|
| | | Oh | planar | Tri |
| Prism | | | | |
| $MX_6$ | 1 | 1 | 1 | 1 |
| $MX_5Y$ | 1 | 1 | 1 | 1 |
| $MX_4Y_2$ | 2 | 2 | 3 | 3 |
| $MX_3Y_3$ | 2 | 2 | 3 | 3 |

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Now, let us look into how he distinguished between primary and secondary valency. For example, he treated cobalt 3 chloride with excess of ammonia and he got a compound having composition, this one hexamine cobalt 3. So in this case, what happens after making this compound where 6 ammonia are there, he treated that one with excess of silver nitrate and he could get three equivalents of silver chloride precipitating out, thereby he said 6 ammonia secondary valency and 3 three chlorides are primary valency.

And again, he generated with the different ratios of chloride and ammonia and in the second one he took 5 ammonia and he ended up having one chloride inside. So, one chloride becomes secondary valency and then two were primary valency. As a result, when he treated with silver nitrate, he could observe precipitation of two equivalents of silver chloride. Similarly, when he had 4 ammonia inside the coordination sphere along with the two chloride, so one chloride was primary valency.

As a result, one silver chloride was precipitated and when he just treated cobalt chloride with three equivalents of ammonia he got a neutral complex having 3 chloride and 3 ammonia as secondary valency and as a result there was no precipitation. So, using this one, again he proposed all of them have octahedral geometry. He could clearly distinguish between secondary valency and primary valency.

For that one, there was no answer from chain theory proposed by Blomstrand and Jorgensen. Despite all this work, the rivalry continued and Jorgensen was not ready to accept. He went on criticizing Werner's work and then similar work he undertook with platinum compounds.

So, he made a platinum compound of this type here and in this one, what happens he could get four equivalents of silver chloride coming out in this one.

Similarly, when he tried this one, he got the three equivalents of silver chloride coming out. So, he went on making all these compounds. And if you see here in this one, tetrachloroplatinate in this one we do not have any ammonia ligands and all chlorides are secondary valency and it is a square planar complex we know and here when he treated with silver nitrate, there was no preparation of silver chloride.

So now he had a dilemma of establishing either tetrahedral geometry or square planar geometry for this one. Let me first come to the establishment of octahedral geometry for secondary valency 6. So when you have coordination number 6, you have three options or three geometries at your disposal; one is hexagonal planar, one is trigonal prismatic and one is octahedral. This is trigonal prismatic and this is trigonal antiprismatic.

The trigonal antiprismatic you can call it as octahedral. So, then he made a homoleptic complex having one type of ligand $MX_6$ and in this one when you try to fit into these geometries all the geometries gave only one isomer. So, here it is inconclusive and option is open here, you can have any one of these things. So, next he made a complex having this composition $MX_5Y$.

Again when he put into all these things, he ended up getting only one isomer and when he attempted the experimentally also he ended up with one isomer but he was very inconclusive in arriving at an appropriate or right geometry for this one with coordinates number 6. It worked out very nicely when he made a metal complex having this composition like $MX_4Y_2$. So, here again he started fitting this one to identify how many isomers are possible with each structure.

So, he tried here, he got three structures here, of course you can try using 4 X and 2 Y ligands and you will end up with three isomers here and same thing is true in case of trigonal prismatic geometry also. You will end up with three isomers, but in case of octahedral geometry you will end up with only two isomers. And in fact, when he made several attempts to make different possible isomers of octahedral complex having composition of $MX_4Y_2$ he could succeed only in making two isomers, not three or more.

Therefore, he concluded that probably preferred geometry is octahedral and not trigonal prismatic or hexagonal planar. So, further evidence came when he made this molecule or this complex having this kind of composition like $MX_3Y_3$. So**,** two type of ligands in 1:1 ratio or in 3:3. So, with this one, what happens when he again tried experimentally with this kind of composition, he ended up with only two isomers.

And again, when you try to fit into these geometries, you end up getting 3 isomers in case of hexagonal planar and also you get 3 isomers in case of trigonal prismatic, but when you try to fit in this composition, you will end up with only two isomers. Now, we know that they are facial and meridional. And again, when he tried experimentally he could get only two isomers with this kind of composition.

With these evidences, he concluded beyond any doubt that when the coordination number is 6 or secondary valency is 6, a complex is going to be assuming octahedral geometry where the central metal ion will be surrounded by 6 ligands in an octahedral fashion. So, this is how he established octahedral geometry and Jorgensen believed in only trivalency and he never believed, he severely criticized, that an ion or a metal ion or any atom can never have 6 coordination, being a very true conservative.

And having more love towards organic chemistry, wherein organic chemistry we know that when the carbon is there, you do not go beyond tetrahedral geometry. So, he was not ready to accept but still he was proposing and he was trying to make popular his theory. And in fact, in 1907 his name was also sent for Nobel Prize. And that time the other eminent scientists' names came into picture were Nernst, Rutherford, Buchner and Werner, and another Werner contemporary Vollard **(23:47).**

So, these six people names were sent and Nobel committee was not convinced that neither Jorgensen's theory nor Werner's theory is complete and they can explain all the properties and eventually in 1907 Buchner was given a Nobel Prize for his cell less fermentation process and of course we are all familiar with that name because we use Buchner funnel for filtration when we got some precipitate.

So, let me stop at this juncture and continue telling interesting story of discovery of coordination compounds by Werner and how eventually he established many more interesting aspects using his coordination theory. Until then have an excellent time of reading chemistry.