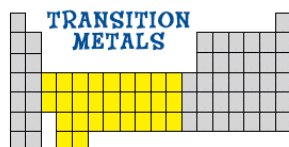


Where are transition metals on the periodic table?

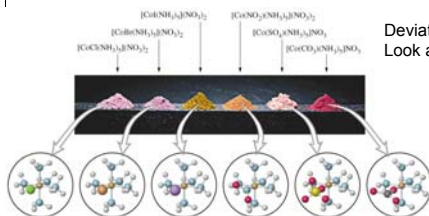


All of these elements have **partially filled d or f shells** in their elemental form or in any of their common oxidation states.



A general approximation for d-block elements involve the progressive filling of the d-orbitals.

Deviations exist to this pattern. Look at the Cr and Ni triads.



Electron configurations of TMs

s block		d block										p block					18
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1A	2A	3A	4A	5A	6A	7A	8A	9A	10A	11A	12A	13A	14A	15A	16A	17A	18A
3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38
39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56
57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74
75	76	77	78	79	80	81	82	83	84	85	86	87	88	89	90	91	92
93	94	95	96	97	98	99	100	101	102	103	104	105	106	107	108	109	110
111	112	113	114	115	116	117	118	119	120								

d- block elements anomalies are indicated in **red**

Row 1

Row 2

Row 3 (filled 4f)

Sc [Ar]4s² 3d¹,
 Ti [Ar]4s² 3d²,
 V [Ar]4s² 3d³,
Cr [Ar]4s¹ 3d⁵,
 Mn [Ar]4s² 3d⁵,
 Fe [Ar]4s² 3d⁶,
 Co [Ar]4s² 3d⁷,
 Ni [Ar]4s² 3d⁸,
Cu [Ar]4s¹ 3d¹⁰,

Y [Kr]5s² 4d¹,
 Zr [Kr]5s² 4d²,
 Nb [Kr]5s¹ 4d⁵,
Mo [Kr]5s¹ 4d⁵,
 Tc [Kr]5s² 4d⁵,
Ru [Kr]5s¹ 4d⁷,
Rh [Kr]5s¹ 4d⁸,
Pd [Kr]5s⁰ 4d¹⁰,
Ag [Kr]5s¹ 4d¹⁰,

Zr [Xe]6s² 5d²,
 Ta [Xe]6s² 5d³,
W [Xe]6s² 5d⁴,
 Re [Xe]6s² 5d⁵,
Os [Xe]6s² 5d⁶,
Ir [Xe]6s² 5d⁷,
Pt [Xe]6s¹ 5d⁹,
Au [Xe]6s¹ 5d¹⁰,

Zn [Ar]4s² 3d¹⁰,

Cd [Kr]5s² 4d¹⁰,

Hg [Xe]6s² 5d¹⁰,

Row 4 are primarily not naturally occurring.

You MUST know the exceptions!

Valence Electrons in TM compounds

This is VERY important!

A general rule for TM compounds:

The valence electron configuration of M^{X+} is $d^n = NVE - \text{oxidation state}$

CrCl_2 : Cr^{2+} $d^n = NVE - \text{oxidation state} = 6 - 2 = d^4$ **IT IS NOT $3d^3 4s^1$**

CrCl_3 : Cr^{3+} $d^n = NVE - \text{oxidation state} = 6 - 3 = d^3$

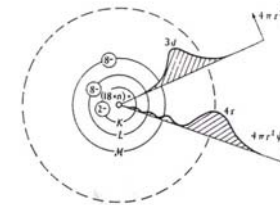
$\text{Cr}(\text{CO})_6$: Cr^0 $d^n = NVE - \text{oxidation state} = 6 - 0 = d^6$

Does this look intriguing? Cr is "zero valent" like Cr metal!
But it also has an electron configuration of d^6 .

$[\text{CoCl}_4]^-$: Co^{3+} $d^n = NVE - \text{oxidation state} = 9 - 3 = d^6$

$[\text{Re}_2\text{Br}_8]^{2-}$: Re^{3+} $d^n = NVE - \text{oxidation state} = 7 - 3 = d^4$

Why only d-electrons?



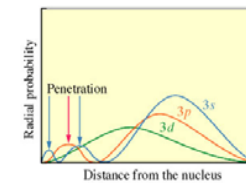
Very simply the relative energies of the nd , $(n+1)s$, and $(n+1)p$ orbitals.

What do you already know from 331?

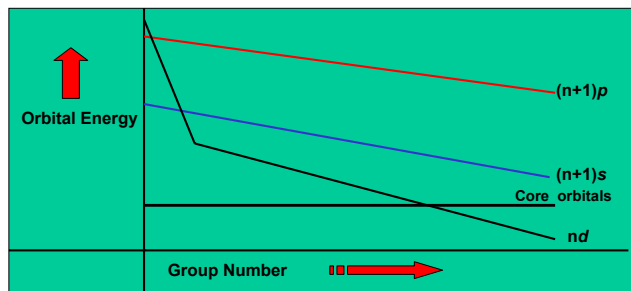
Generally, Z_{eff} increases across the periods **WHY?**

BUT THE Z_{eff} CHANGE AFFECTS THE n d-ORBITALS MORE THAN $(n+1)$ s and p.

They are closer to the nucleus.



d-orbital energy



The orbital energy of a nd orbital decreases faster than that of the $(n+1)s$ which in-turn decreases faster than the $(n+1)p$ when going across the period.

This is implied by what we see in the electron configuration of Ga; $[\text{Ar } 3d^{10}]4s^24p^1$. For Ga the $3d^{10}$ are part of the "core". This means the electron configuration of Ga mirrors that of B and Al, " s^2p^1 "

Physical Properties of TMs

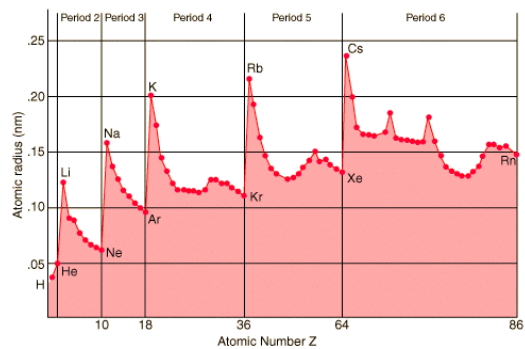
1. Almost all TMs are hard, ductile, malleable, high melting, and exhibit high electrical and thermal conductivities.
2. Relative to Group I and II metals TMs are much HARDER and less VOLATILE. The heats of atomization (ΔH_{atom}) are much higher than other main group metals.

Important experimental observation:

$$\Delta H_{\text{atom}} (\text{row 2 and 3 TMs}) > \Delta H_{\text{atom}} (\text{row 1 TMs})$$

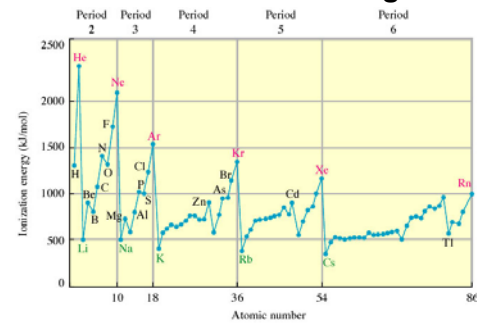
THIS IS IMPORTANT IN ACCOUNTING FOR THE INCREASED PROPENSITY FOR M-M BONDING IN COMPOUNDS OF HEAVY TMs.

TM Atomic Radii



TMs have smaller radii than Group I and II metals. There is a decrease in size with increased atomic number but not as dramatic as see for main group metals.

TM 1st Ionization Energies



IE₁ of TMs are higher than Group 1 and 2 metals but vary far less than those of typical elements (look at K through Kr).

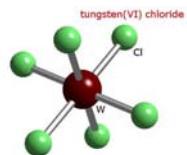
IE increases with Z across a period with small variations (don't worry about them)

Chemical Properties of TMs

Given the high ΔH_{atom} and IE of TMs they tend to be less reactive than Group II metals. Yet, they will react with O_2 , S, and halogens if they are heated with these elements.



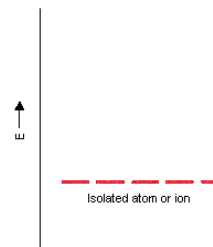
Blue-black crystals



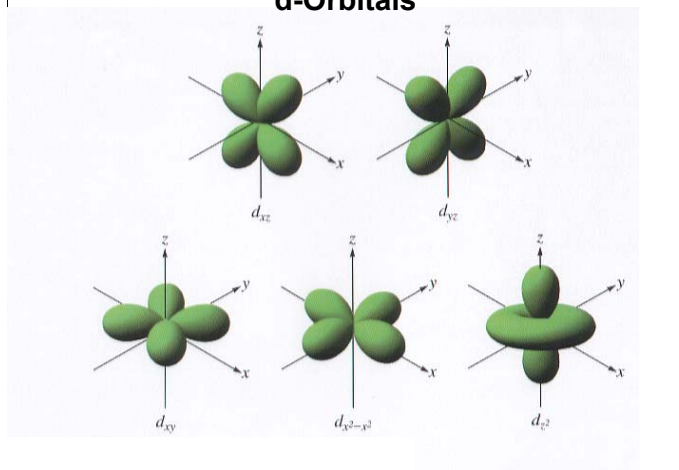
TM compounds

TM compounds are often coloured. Colours originate from electronic transitions between different d-orbitals of the same principle QN.

Wait....aren't all d orbitals the same energy?



d-Orbitals



TM magnetism

Many TM compounds are **paramagnetic**: this is because of partially filled d-orbitals and the resulting unpaired electrons.

Increasing field strength 



Cobalt(II) chloride hexahydrate

3 unpaired electrons which align their spins with a large applied magnetic field and are drawn into it.

For a more complete discussion on magnetism see handout later.

DIAMAGNETIC



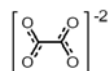
PARAMAGNETIC



of UPE is commonly measured experimentally using a Gouy Balance, NMR spectroscopy.

[More on this later.](#)

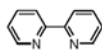
TMs have a wide range of reactivity



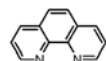
oxalate, "ox"



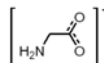
pyridine, "py"



bipyridine, "bpy"



phenanthroline, "phen"



glycinate, "gly"

TMs are Lewis acids and will accept electrons from Lewis bases.

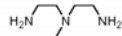
We refer to these Lewis bases as ligands. (Latin, "to tie or bind")



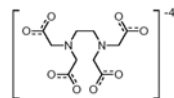
ethylenediamine, "en"



diethylenetriamine, "dien"



triethylenetriamine, "tren"



ethylenediamine tetraacetate, "edta"

TM oxidation states

TMs have numerous available oxidation states. This is VERY important as it sets apart their chemistry from the main group elements.

It is also very difficult to discuss this comprehensively.

Generalities:

- i) Early and Late Transition metals have few oxidation states.
 - Early TMs have very few *d* electrons to loose.
 - Late TMs have high Z_{eff} and loss of electrons is difficult.
- ii) High oxidation state TMs tend to form covalent molecules rather than simple ionic salts.

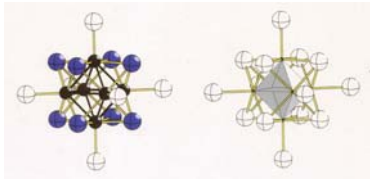
High oxidation states are most stable for 2nd and 3rd row TMs.

Examples of the influence of TM oxidation states.

TiCl_2 and TiCl_3 are solids like SnCl_2 , TiCl_4 is a molecular liquid like SnCl_4 . Mn_2O_7 is an explosive oil but Re_2O_7 melts at 220°C and OsO_4 is a volatile solid. The latter two compounds are covalent substances and the +7 and +8 oxidation states are "formal".

TM oxidation states con't

- iii) The Chemistry of 1st row TMs is dominated by M^{2+} and M^{3+} ions. There is extensive solution chemistry involving redox equilibria, complex formation, and precipitation.
- iv) The Chemistry of 2nd and 3rd row TMs is not as straightforward.
-lower oxidation states are dominated by M-M interactions ("MoCl₂" below)



- High oxidation states form molecular species and covalent bonds.
- Aqueous Chemistry is complicated and rarely involves simple, monoatomic species.

Ligands and TM Oxidation States

Ligands that stabilize low oxidation states.

Two common ligands tend to favor metals of low ox. State.
Carbon monoxide (CO) and the isoelectronic cyanide ion (CN⁻)
(a detailed discussion of M-CO bonding will follow shortly)

Ligands that stabilize "normal" oxidation states.

Most ligands fall into this category.

Ligands that stabilize HIGH oxidation states.

Think back to the fluorine complexes of Xe...this will help you understand. Generally TMs will adopt high Ox. States if they are coordinated to fluoride or oxide ions.

Coordination Chemistry

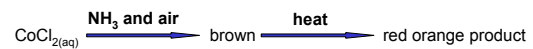
Rodgers Chapter 2

These compounds are challenging to chemists...hence the term complex has come to be associated with them.

These compounds appear to violate the rules of "valence".

An example of the puzzlement.

Let's go back to 1800 when Tassaert and Fremy studied Co(II) reacting with NH_3 .



Fremy successfully demonstrated that Co(II) was oxidized to Co(III) but there were 6NH_3 molecules associated with each Co.

Questions arise....

Chemical Controversy

$\text{CoCl}_{2(aq)}$ $\xrightarrow{\text{NH}_3 \text{ and air}}$ a lot of coloured products

Systematic nomenclature by Frémy according to color

Prefix	Color
Flavo	brown-yellow
Croceo	yellow-orange
Luteo	yellow
Purpureo	purple
Roseo	pink-red
Praseo	green
Violeo	violet

ca. 1870 Kettentheorie (**Blomstrand** and **Jørgensen**)
based on Valence numbers

Sophus Mads Jørgensen, Professor at the University of Copenhagen

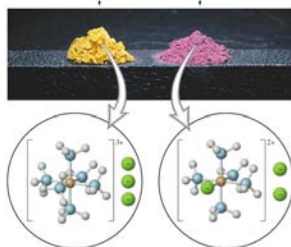
Alfred Werner



Golden orange



Purple



Werner developed his theory of coordination chemistry at the age of 26, received the 1913 Nobel Prize for chemistry and in 25 years supervised 200 PhD students and published syntheses for in excess of 8000 complexes.

How does Werner's work manifest itself now?

I. Every metal of a particular *Oxidation State* has a definite *Coordination Number*.

The oxidation state is "satisfied" or "balanced" by the presence of anions.

The coordination number can be is "satisfied" not only by the presence of anions, but also by electron-pair donating, neutral molecules like N, O, S, P.

THIS SHOULD LOOK FAMILIAR!

The **oxidation state** of a metal center is defined by its electronic configuration.

The **coordination number** of a metal center is defined as the number of atoms directly bonded to the metal center.

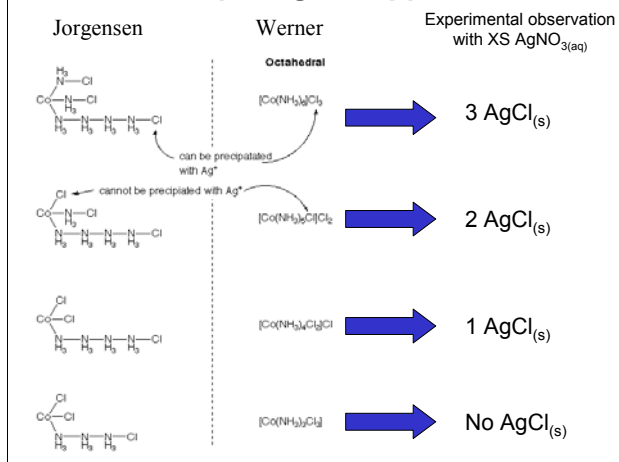
This portion of the theory may be viewed as the "constitution" of a coordination compound

II. The bonds of ligands are "fixed" in space.

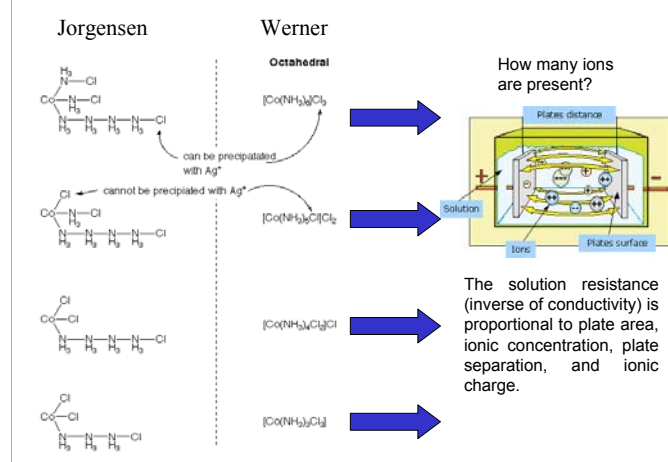
This postulate gives rise to fixed geometric structures of coordination compounds and the possibility of isomers.

This portion of the theory may be viewed as the "configuration" of a coordination compound

Comparing the approaches



How else could this have been tested



Configuration in coordination compounds and isomer counting

How can we explain that there are two different complexes with the formula $[\text{CoCl}_2(\text{NH}_3)_4]^+$

One is **GREEN**.....the other is **VIOLET**

What if the complex of the formula ML_4X_2 was planar?

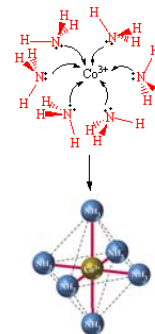


Not all the ligands are equivalent how many orientations will there be?

Why do these complexes form?

Recall that based upon the work of Lewis and Sidgwick a chemical bond requires the "sharing" of an electron pair.

Acid (LA) : electron pair acceptor Base (LB): electron pair donor



From this it can be drawn that metals behave as Lewis acids and Ligands as Lewis bases.

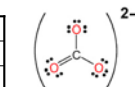
A bond like that seen in $[\text{Co}(\text{NH}_3)_6]^{3+}$ is a "coordinate-bond" or "dative-bond". This used to be denoted with \longrightarrow . This is no longer the case.

This is because there is no fundamental difference between a "coordinate-bond" and a polar covalent bond.

Yet there is a difference in that a **covalent bond undergoes homolytic cleavage** and a **dative bond undergoes hetrolytic cleavage**.

Typical Monodentate Ligands

F ⁻	fluoro
Br	bromo
I ⁻	iodo
CO ₃ ²⁻	carbonato
NO ₃ ⁻	nitrato
SO ₃ ²⁻	sulfito
S ₂ O ₃ ²⁻	thiosulfito
SO ₄ ²⁻	sulfato
CO	carbonyl
Cl ⁻	chloro
O ²⁻	oxo
O ₂ ²⁻	peroxo
OH ⁻	hydroxo
NH ₂ ⁻	amido
CN ⁻	cyano
SCN ⁻	thiocyano
NO ₂ ⁻	nitro

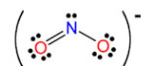
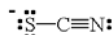
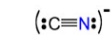


Can be bidentate

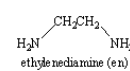
Common bridging ligands.

Common bridging ligands. That are also ambidentate.

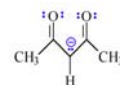
H ₂ O	aqua
NH ₃	ammine
CH ₃ NH ₂	methylamine
P(C ₆ H ₅) ₃	triphenylphosphine
As(C ₆ H ₅) ₃	Triphenyl arsine
N ₂	dinitrogen
O ₂	dioxygen
NO	nitrosyl
C ₂ H ₄	ethylene
C ₅ H ₅ N	pyridine



Typical multidentate ligands



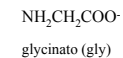
ethylenediamine (en)



acetoacetonato (acac)

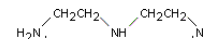


oxalato (ox)



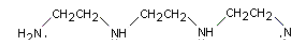
glycinato (gly)

Tridentate Ligand:



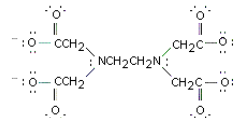
diethylenetriamine (dien)

Tetradentate Ligand:



triethylenetetraamine (trien)

Hexadentate Ligand:



ethylenediaminetetraacetate (EDTA)

Ligand Nomenclature Rules

1. Anionic ligands all end in *-o*.
2. Neutral Ligands are named as the neutral molecule.
3. There are some special names for neutral ligands.
4. Cationic ligands end in *-ium*.
5. Ambidentate ligands are indicated by:
 - i) using special names for the two forms (nitro $-\text{NO}_2^-$ and nitrito $-\text{O}-\text{NO}$)
 - ii) placing the symbol for the coordinating atom in front of the ligand name (s-thiocyanato or N-thiocyanato).
6. Bridging ligands are indicated by placing μ^- before the ligand name.

Examples of these rules may be found on your handout.

Rules for Simple Coordination Compounds

1. Name the cation first, then the anion.
2. List the ligands alphabetically.
3. Indicate the number (2,3,4,5,6) of each type of ligand by:
 - The prefixes di, tri, tetra, penta, hexa for:
 - a) All monoatomic ligands.
 - b) Polyatomic ligands with short names.
 - c) Neutral ligands with special names.
 - The prefixes bis, tris, tetrakis, pentakis, hexakis for:
 - a) Ligands whose names contain a prefix of the first type (di, tri, etc.)
 - b) Neutral ligands without special names.
 - c) Ionic ligands with particularly long names.
4. If the anion is complex, add the suffix *-ate* to the name of the metal. (Often the *-ium* or other suffix of the normal name is removed prior to adding *-ate*. Some metals such as copper, iron, gold, and silver use the Latin stem names and become cuprate, ferrate, aurate, and argenate respectively.)
5. Put the ox. state in roman numerals in parentheses after the name of the central metal.

Examples of Naming

$[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]\text{Br}_3$	amine x 5 water x 2	cobalt (III)	bromide
$[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$	amine x 5 bromine x 1	cobalt (III)	bromide
$[\text{Co}(\text{NH}_3)_5\text{Br}](\text{SO}_4)$	amine x 5 bromine x 1	cobalt (III)	sulfate
$[\text{Co}(\text{NH}_3)_5(\text{SO}_4)]\text{Br}$	amine x 5 sulfate x 1	cobalt (III)	hydrogen sulfate

Pentaaminediaquacobalt (III) bromide

Pentaaminebromocobalt (III) bromide

Pentaaminebromocobalt (III) sulfate

Pentaaminesulfatocobalt (III) bromide

More examples can be found in Rodgers Chapter 2 P. 20-25.

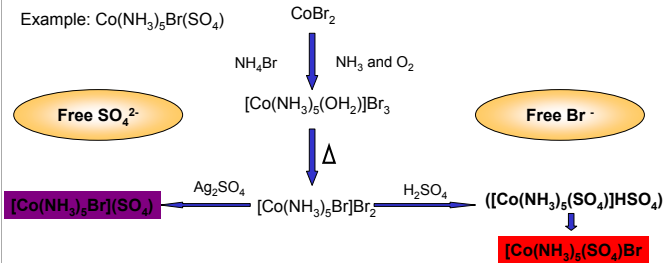
Structural Isomerism

Definition. Structural isomers have the identical composition and differ in M-L linkages.

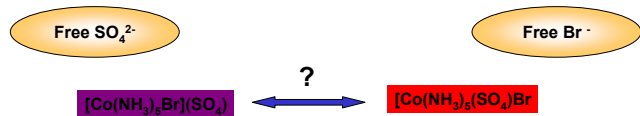
This class of isomers was crucial to the realization of Werner's premise regarding the constitution of coordination complexes.

Structural isomers may be divided into sub-classes of: **ionization isomers, coordination isomers, and linkage isomers.**

Ionization isomers *like hydration*: 2 different ions are obtained when dissolved in solution.



How do we know the difference?

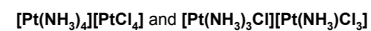


Coordination Isomers

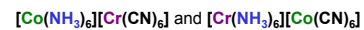
Coordination isomers are possible when both the anion and cation contain metal ions. As a result different distributions of ligands between metal centers result.

Two compounds are known that contain two Pt(II) ions, four ammonia molecules, and four chloride ions.

They are:

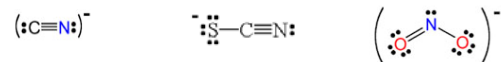


$[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ has the **same ratio of atoms**, but does not have the same overall formula. It is not a coordination isomer of the above compounds.

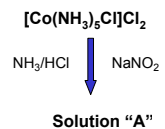


Linkage Isomers

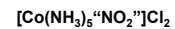
Linkage isomers can exist when one or more ambidentate ligands is bonded to a metal ion.



This type of isomerization was discovered by Jorgensen in 1894.



What's going on?



The nitrite ion can bind in two different ways. Through the O or through the N.

What do the structures look like?

Jorgensen figured this out in 1894.....BUT HOW?
He did not have IR-spectroscopy, X-ray crystallography, etc...

Was he correct?

How can you tell?

Isomerization Summary

Ionization Isomers. 2 different ions are obtained when dissolved in solution. (Same formula.....different solution species.)

This is similar to the Hydration, although in the case of HI isomers differ in the number of coordinated water molecules.

Coordination Isomers. When both the anion and cation contain metal ions different distributions of ligands between metal centers result.

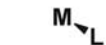
Linkage Isomerism. Bonding of ligands through different modes. A good example of this involves the binding of NO_2 .

Structure of Simple Coordination Compounds

A review of conventions for drawing 3-D structures on paper.



M-L bond in the plane of the page.



M-L bond out of the plane of the page.

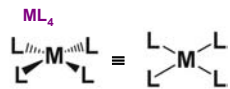


M-L bond into the plane of the page.

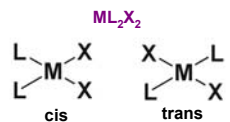
Four Coordinate Complexes



tetrahedral



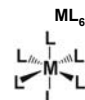
square planar



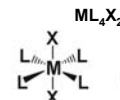
cis

trans

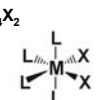
Six Coordinate Complexes



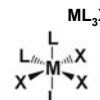
octahedral



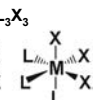
trans-



cis-



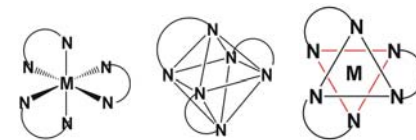
facial (fac)



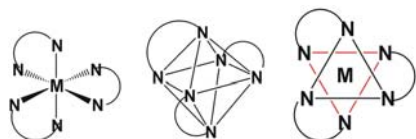
meridional (mer)



These are the same complexes viewed down a face of the octahedron.



Tris-ethylenediamine Chelates



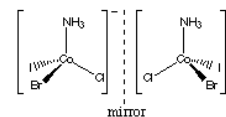
These are the structural representations of ONE optical isomer.

Understanding these structural formulae is crucial to you deciding on chirality.

Optical Isomerization

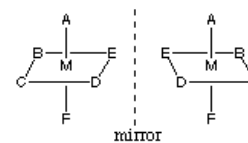
Tetrahedral Geometry

The $[\text{Co}(\text{NH}_3)\text{ClBrI}]^-$ ion is tetrahedral, with four different groups bonded to the cobalt. It has two nonsuperimposable mirror images:



This is the same as you see for organic chemistry.

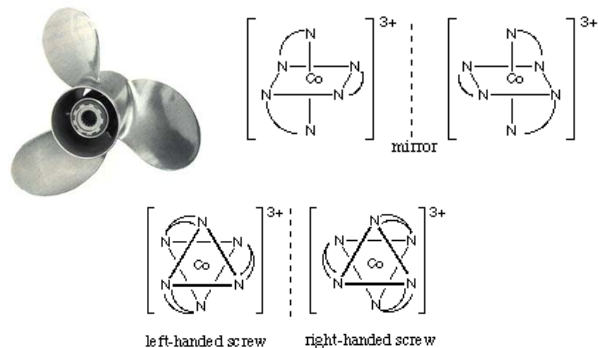
Octahedral Geometry



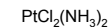
Similarly, an octahedral metal ion bonded to 6 different ligands would be chiral.

Optical Isomerization Con't

Chirality and optical isomerism that does not merely depend on having four different groups attached to a tetrahedral central atom. Tris(ethylenediamine)cobalt(III) ion is chiral, in spite of the fact that the three ethylenediamine ligands are all the same and are themselves symmetrical:



cisplatin



Diaminedichloroplatinum (II)

Cisplatin was first synthesized by M. Peyrone in 1844 and has been called Peyrone's chloride. Its structure was first elucidated by Alfred Werner in 1893.



The trans isomer $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ is therapeutically inactive.

It is possible to distinguish between isomers based on the activity of the two Pt-Cl bonds (expected around 300 cm^{-1} in the IR region). The vibrational spectra of these isomers differ, due to the different symmetries. The point group affiliations for the two isomers are different, and, as it turns out, so are the vibrational selection rules.

Discovery of Clinical application.

In the early 1960's, a series of experiments in the laboratories of Barnett Rosenberg at the Michigan State University found some peculiar results. An experiment designed to measure the effect of electrical currents on cell growth yielded *Escherichia coli* that were 300 times the normal length. This effect was not due to the electrical fields themselves but to a chemical agent that was formed in a reaction between the supposedly inert platinum electrodes and components of the solution. The chemical agent was later determined to be cisplatin.

Tests revealed the compound had prevented cell division, but not other growth processes in the bacteria. **It was approved for cancer treatment in 1978.**

Survey of Ligands

The most efficient method for classifying ligands is by structure.

Specifically, by the number of coordinate (dative) bonds they make with a central metal atom.

Monodentate. *ONE* donation per ligand. This literally means "one-toothed".

Examples. These ligands may be neutral or anionic.

:NR₃, :PR₃, (NR₂), (PR₂), OR₂, SR₂, OR⁻ (including OH), O²⁻, X⁻ (halides)

It is important to note that there is only **ONE** donor atom. BUT, when there are more than one L.P. available these ligands can bridge metal ions.

Note that this is different that in B₂H₆, here each bond is 2 center-2 electron.

Survey of Ligands

Polydentate. *More than ONE* donation per ligand.

Bidentate Ligands. (two donors, two teeth)

When these ligands bind to a single central metal they are said to be "chelating ligands". (This arises from the Greek word for claw.)

Four membered rings. (See Experiment 4 for the different bonding modes of the carboxylate ligand.)

carboxylate

dithiocarbamates

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Survey of Ligands

Bidentate Ligands. (two donors, two teeth) cont'd

Five membered rings.

ethylenediamine (en)

2,2'-bipyridine (bpy)

Six membered rings.

β -diketonates (acetylacetonate, acac)

salicylaldiminato (sal)

My favorite "bidentate" ligand.



Survey of Ligands

Polydentate. *More than ONE* donation per ligand.

Tridentate Ligands. (three donors, two teeth)

Diethylenetriamine

terpyridine (trpy)

Hydrotris(pyrazolyl) borates (TpRR')

Quadradentate

porphyrin

Survey of Ligands

Penta- and higher dentate Ligands.

The most well known hexadentate ligand is ethylenediaminetetraacetate (EDTA^{4-}). It can be protonated and be a pentadentate ligand. (EDTAH^{3-}).

EDTA^{4-}

EDTAH^{3-}

Other examples include:

Crown Ethers

Cryptates

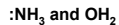
15-crown-5

dibenzo-18-crown-6

Electronic Classification of Ligands

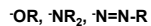
Ligands can be classified in terms of their electronic characteristics and their interaction with a metal center.

Classical or Simple donors. All ligands must be able to donate an electron pair to the metal center (the Lewis acid) to form a σ -bond. These ligands are also known as σ -donors.



π -donors. If a ligand has *more than one electron pair* to donate to the metal center it can form a σ -bond (as above) and if it has the ability to donate more electrons through π -donation.

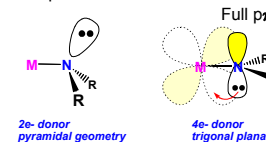
Without question *these ligands can stabilize high oxidation state metal centers.* M^{n+} will be electron deficient and has empty $d\pi$ orbitals to accommodate the extra ligand electrons.



O^{2-} , N^{3-} these are strong π -donors

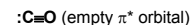
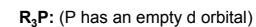
Electronic Classification of Ligands

π -donors. The orbital picture.



π -acid ligands. These ligand donate one electron pair in a σ -bond (as above) and the ability to accept back metal electrons through π -donation.

In this case the electrons are clearly coming from the metal center and the metal center MUST be electron rich.



Draw the orbital cartoon!

Recall the HSAB concept of CHEM331. (R-C pp. 141-149; 450-451).