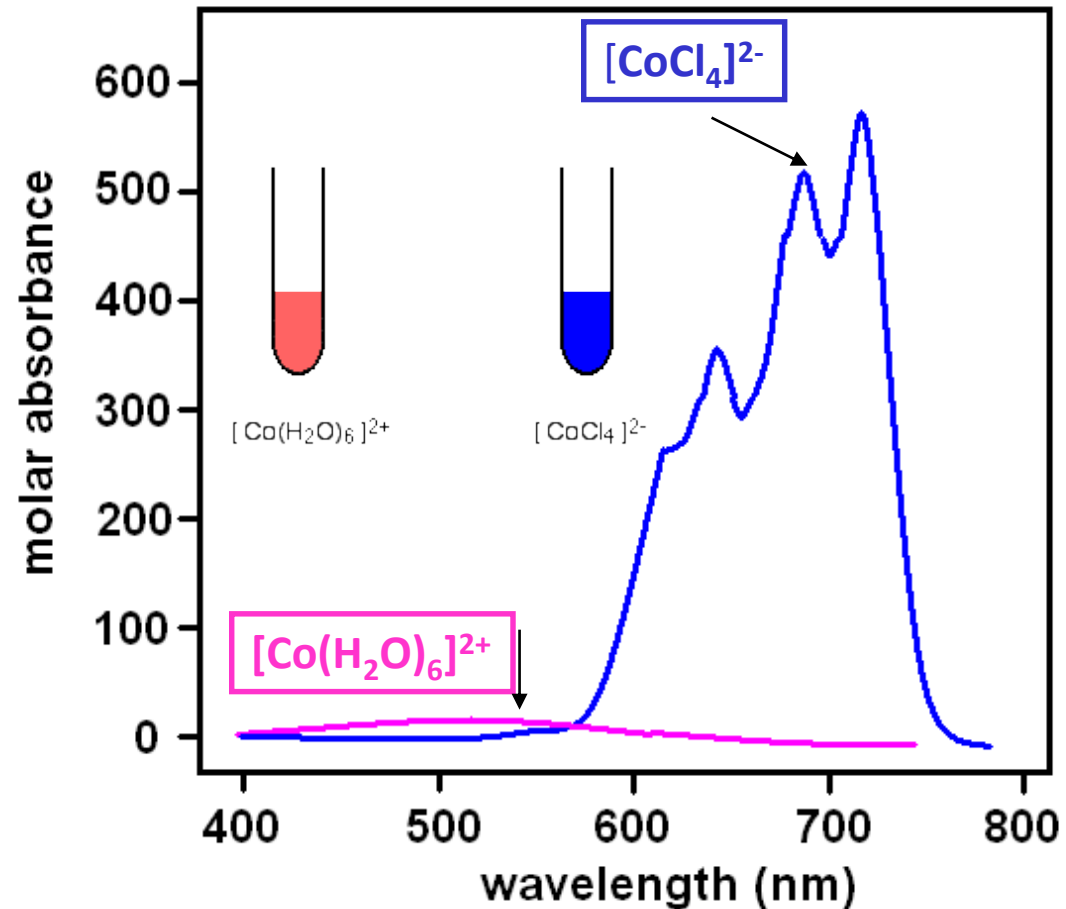
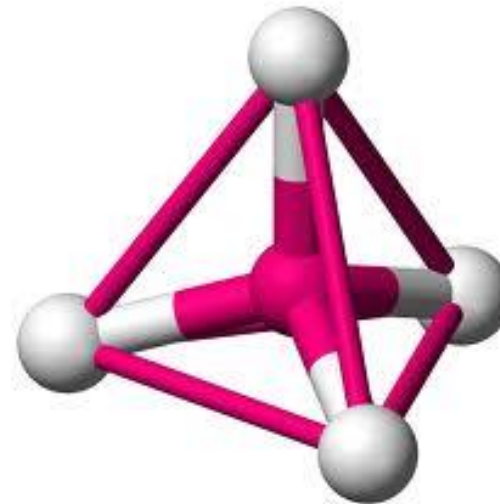


Lecture 5
Crystal field theory and organometallic chemistry

The spectra of octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and tetrahedral $[\text{CoCl}_4]^{2-}$ ions:



Intense d-d bands in the blue tetrahedral complex $[\text{CoCl}_4]^{2-}$, as compared with the much weaker band in the pink octahedral complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. This difference arises because the T_d complex has no center of symmetry, helping to overcome the $g \rightarrow g$ Laporte selection rule.



Classification of intensities of electronic transitions

Transition type	Example	Typical values of ϵ /m ² mol ⁻¹
-----------------	---------	--

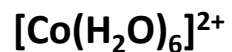
Spin forbidden,
Laporte forbidden
(partly allowed by **spin-orbit coupling**)



0.1



Spin allowed (octahedral complex),
Laporte forbidden
(partly allowed by **vibronic coupling and d-p mixing**)



1 - 10



Spin allowed (tetrahedral complex),
Laporte allowed (but still retain some original character)



50 - 150



Spin allowed,
Laporte allowed
e.g. **charge transfer** bands



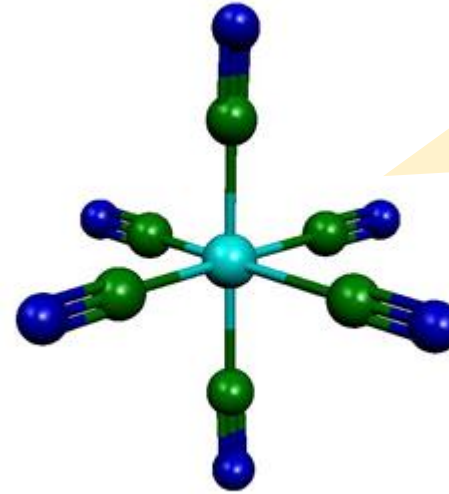
1000 - 10⁶



Relaxing the selection rules

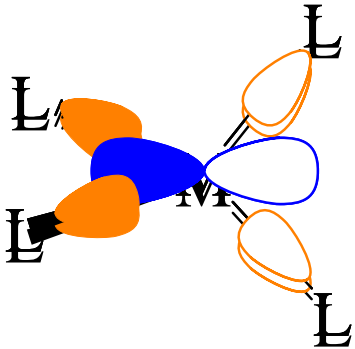
Vibronic coupling

An octahedral complex possesses a centre of symmetry, but molecular vibrations result in its temporary loss, which partially relaxes the Laporte selection rule.

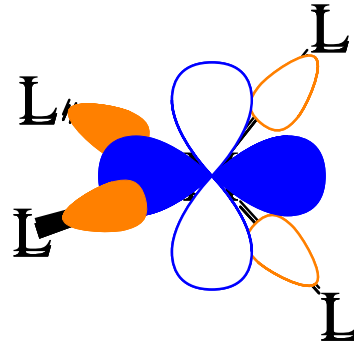


Molecules are not rigid but always vibrating. During this vibration, centre of inversion is temporarily lost

Mixing of states



A metal p -orbital overlaps with ligand orbitals



A metal d -orbital overlaps with the same ligand orbitals

As the molecular orbitals are actually mixtures of d and p -orbitals, they are partially allowed as $\Delta l = \pm 1$

Charge-transfer bands

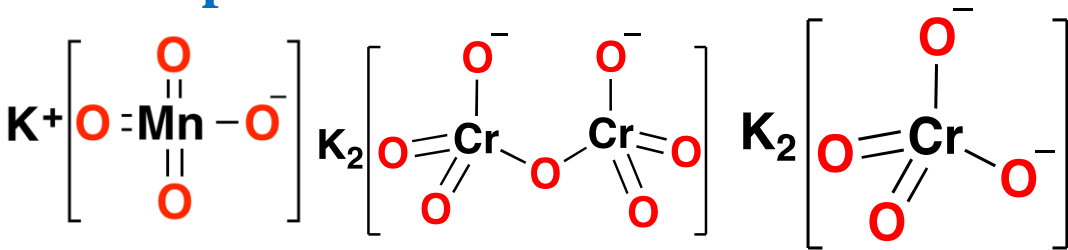
What is a charge-transfer transition?

There are many compounds where either the metal ion is highly oxidizing and the ligands are reducing or that the metal ion is highly reducing and the ligands are oxidizing. In such cases there occurs transfer of charge. (i.e electron) from the reducing partner to the oxidizing partner. The metal ion may not possess d-electrons.

What is “Ligand-To-Metal (LMCT)” Charge Transfer?

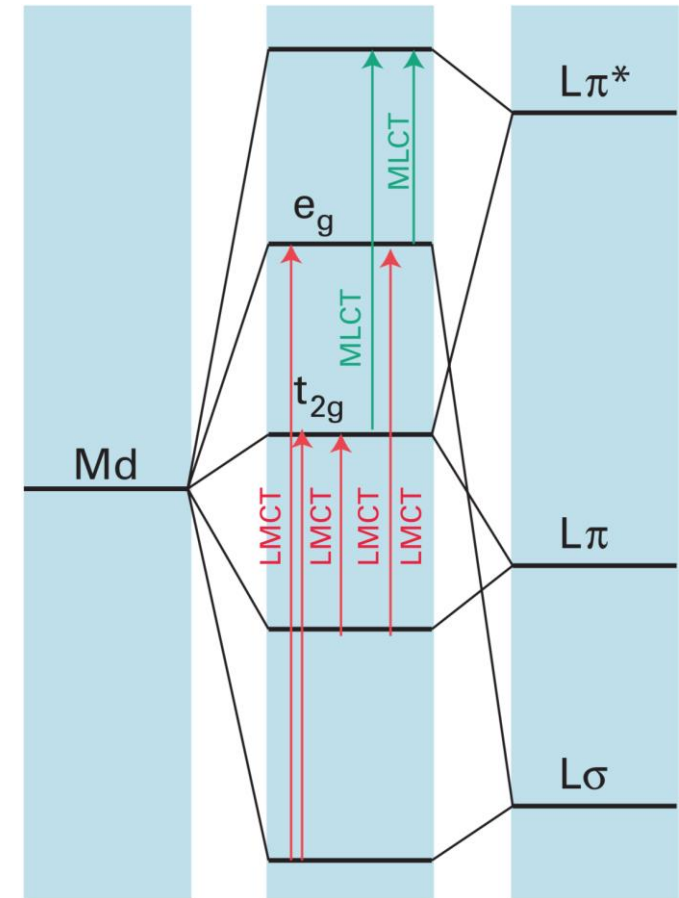
Ligand-to-metal charge-transfer transitions are observed in the visible region of the spectrum when the metal is in a high oxidation state and ligands contain nonbonding electrons.

Examples of LMCT transitions



- | | | | |
|-----|----------|--------------|----------|
| (a) | t_{2g} | \leftarrow | π |
| (b) | e_g | \leftarrow | π |
| (c) | t_{2g} | \leftarrow | σ |
| (d) | e_g | \leftarrow | σ |

Possible LMCT transitions



A summary of the charge-transfer transitions in an octahedral complex.

Charge-transfer bands



LMCT transitions are *usually* in the ultraviolet region. They occur in the visible or near-ultraviolet if:

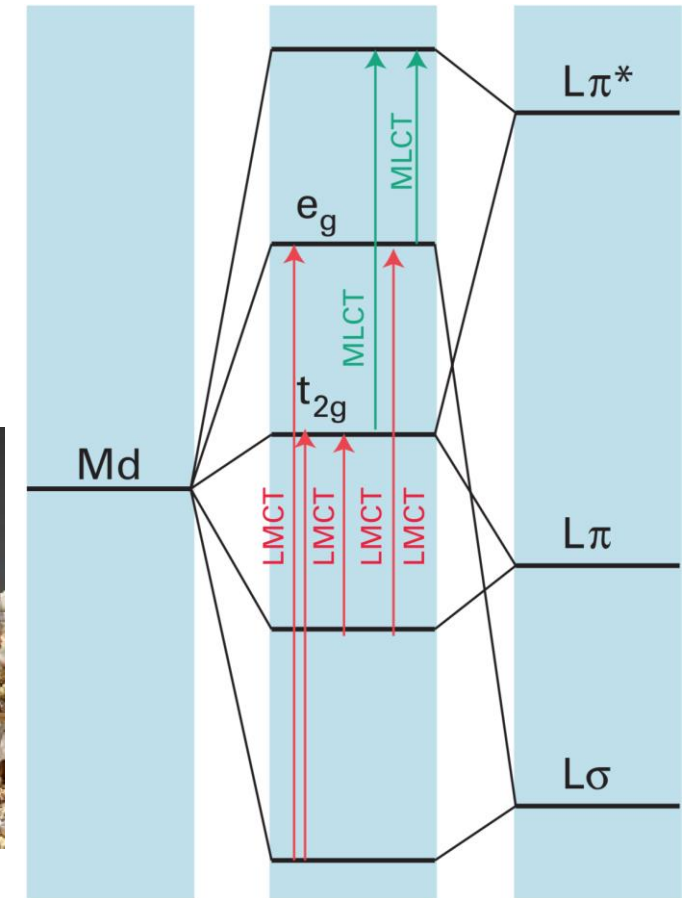
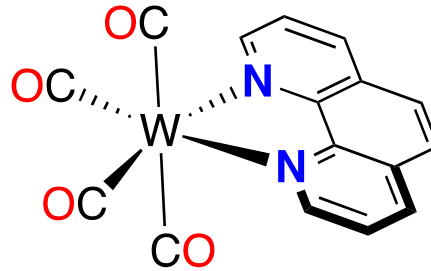
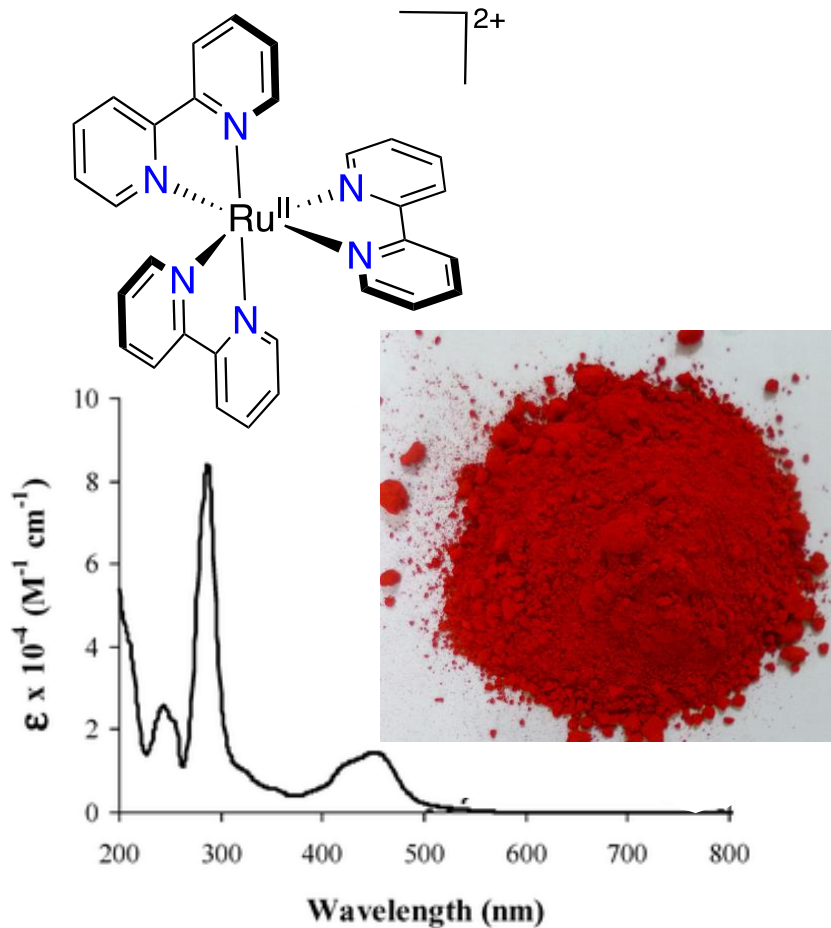
- Metal center is easily reduced. For example when a metal is in high oxidation state.
- Ligand is easily oxidized.

	TiO_2	VO_4^{3-}	CrO_4^{2-}	MnO_4^-
	Ti^{4+}	V^{5+}	Cr^{6+}	Mn^{7+}
d^0	in far UV	$\sim 39500 \text{ cm}^{-1}$	$\sim 22200 \text{ cm}^{-1}$	$\sim 19000 \text{ cm}^{-1}$
	white	white	yellow	purple
	more easily reduced			

Charge-transfer bands

What is “Metal-To-Ligand (MLCT)” Charge Transfer?

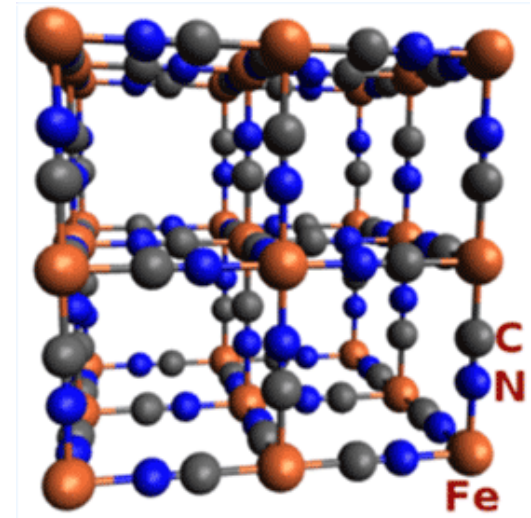
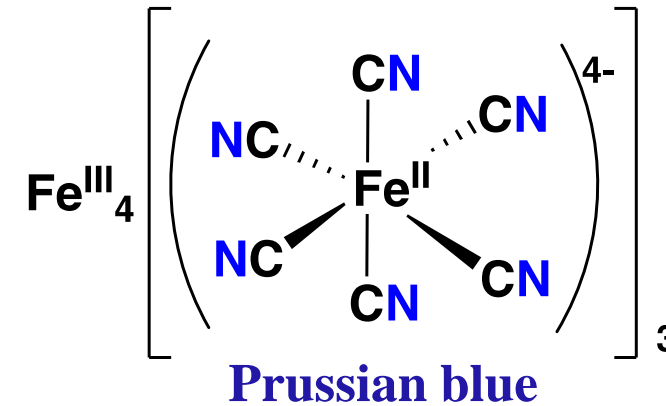
Charge-transfer transitions from metal to ligand are observed when the metal is in a low oxidation state and the ligands have low-lying acceptor orbitals (like π^* orbitals), especially aromatic ligands.



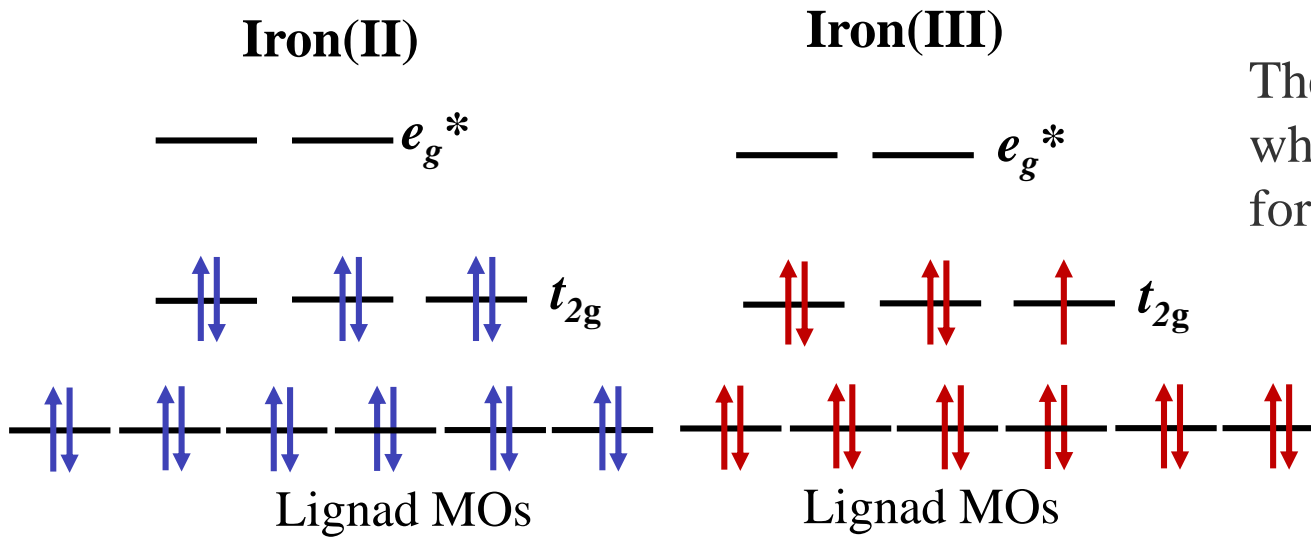
A summary of the charge-transfer transitions in an octahedral complex.

What is “Metal-To-Metal” Charge Transfer?

When there are two or more metal centres close together, spectral transitions can occur between the orbitals based on one metal and those on the other. An interesting set of complexes is those with one metal in two different oxidation states. Such complexes are often intensely coloured.



The name Prussian blue originated in the 18th century, when the compound was used to dye the uniform coats for the Prussian army.



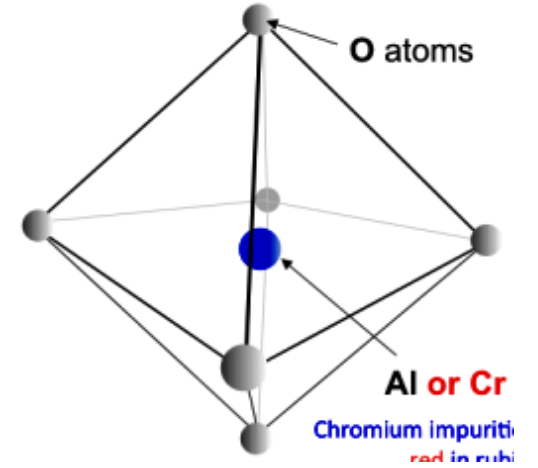
In Prussian blue, $\text{Fe}^{\text{III}}_4[\text{Fe}^{\text{II}}(\text{CN})_6]_3$, the iron(III) ions are octahedrally surrounded by the nitrogen atoms of the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ion. The blue colour is due to transitions from a t_{2g} orbital on iron(II) in the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ ion to the t_{2g} and e_g^* orbitals on iron(III).



Origin of color in Gem Stones : Ruby and Emerald



Ruby is Al_2O_3 containing around 0.2—1 atom per cent Cr^{3+} ions in place of the Al^{3+} ions and its red colour results from the absorption of green light in the visible spectrum as a result of the excitation of Cr 3d electrons



corundum (Al_2O_3) and **Ruby**: corundum with chromium as impurity.



In Emerald, the host structure is beryl, beryllium aluminium silicate, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$, and the Cr^{3+} ion is surrounded by six silicate ions, rather than the six O^{2-} ions in ruby, producing absorption at a different energy.



Peridot

Fe^{2+} replacing Mg^{2+} in 6-coordinate sites in Mg_2SiO_4

Mineral beryl ($\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$), and **Emerald**: Beryl colored green by trace amounts of chromium and/ or vanadium

Problem solving

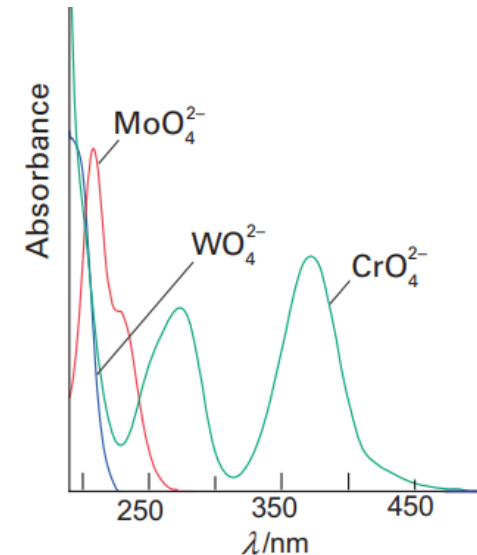
(1) A filter paper moistened with cadmium acetate solution turns yellow upon exposure to H_2S . The transition responsible for the yellow color is

charge transfer

(2) $[\text{CrO}_4]^{2-}$ is deep yellow in colour whereas $[\text{WO}_4]^{2-}$ is colorless. This is due to greater energy required for

(a) d-d transition in the Re compound compared to the Mn compound (b) d-d transitions in the Mn compound compared to the Re compound (c) charge transfer from O to W compared to O to Cr (d) charge transfer from O to Mn compared to O to Re

The energies of the transitions correlate with the order of the electrochemical series, with the lowest energy transitions taking place to the most easily reduced metal ions.



Advantages and Disadvantages of Crystal Field Theory

Advantages over Valence Bond theory

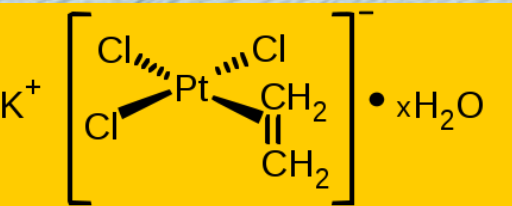
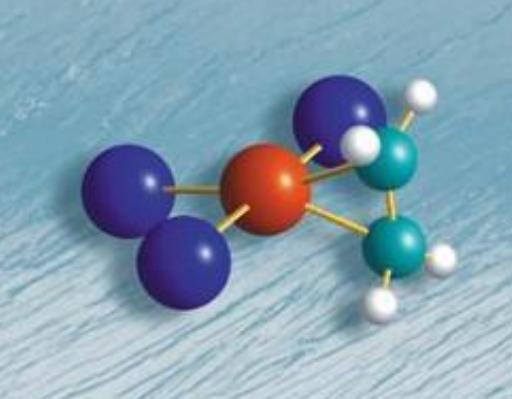
1. Explains colors of complexes
2. Explains magnetic properties of complexes (without knowing hybridization) and temperature dependence of magnetic moments.
3. Classifies ligands as weak and strong
4. Explains anomalies in physical properties of metal complexes
5. Explains distortion in shape observed for some metal complexes

Disadvantages or drawbacks

1. *Evidences for the presence of covalent bonding (orbital overlap) in metal complexes have been disregarded.
e.g Does not explain why CO although neutral is a very strong ligand*
2. *Cannot predict shape of complexes (since not based on hybridization)*
3. *Charge Transfer spectra not explained by CFT alone*

Organometallic Chemistry

The 18 electron rule, Metal Carbonyls and sandwich compounds,
Unique reactions of organometallics and their use in explaining homogeneous catalysis



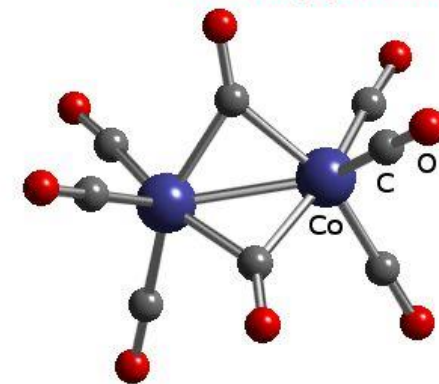
Organometallic Chemistry

An area which bridges organic and inorganic chemistry

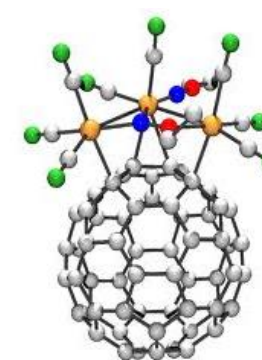
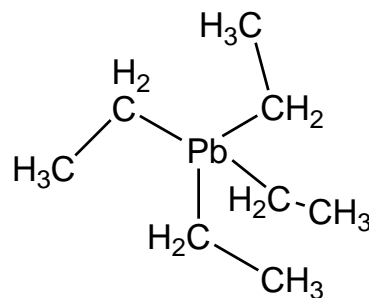
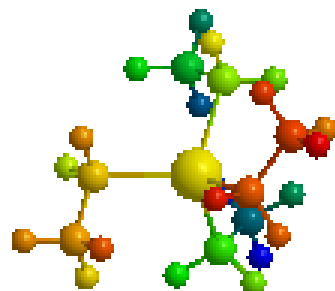
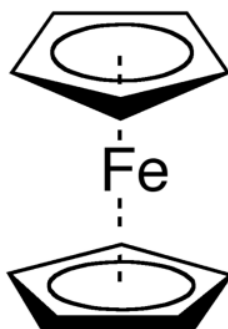
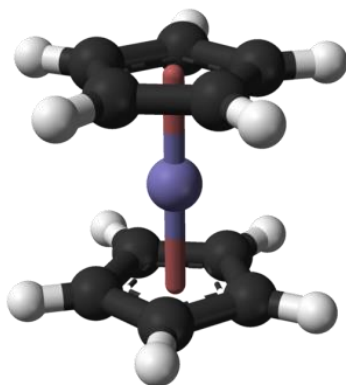
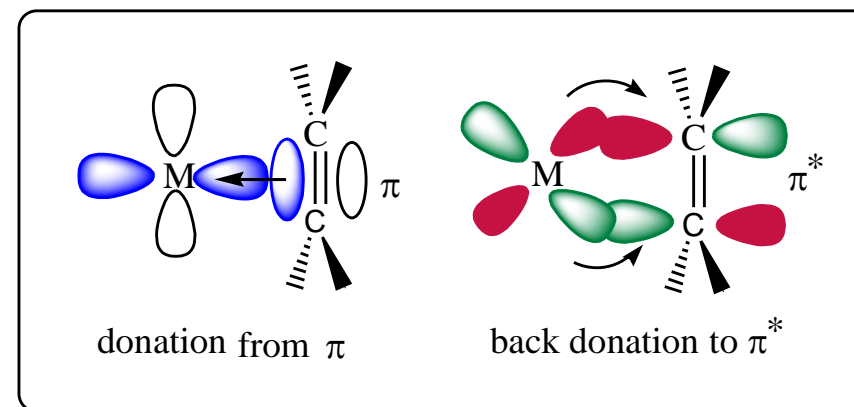
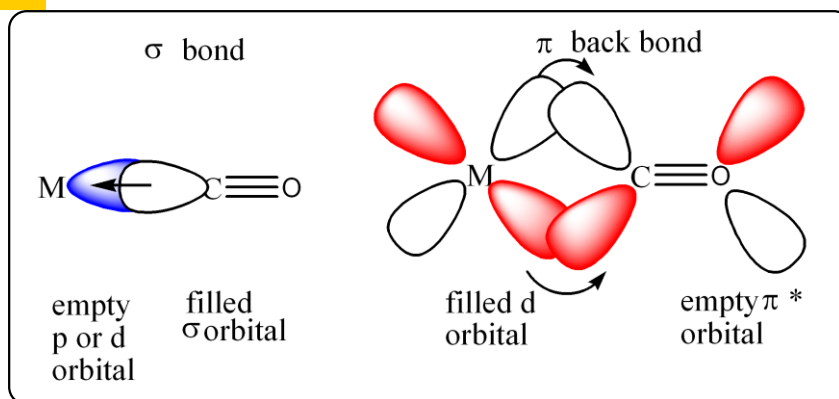
A branch of coordination chemistry where the complex has one or more metal-carbon bonds

M-C bond can be a σ type or π type bond

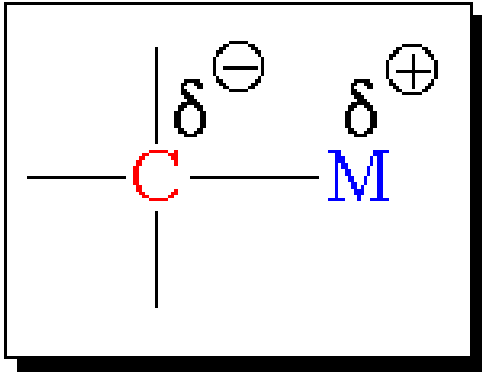
dicobalt(0) octacarbonyl



$\text{Co}_2(\text{CO})_8$



What all compounds are considered as organometallic?



C always more electronegative compared to M

The leading journals of the field define an "organometallic" compound as one in which there is a **bonding interaction (ionic or covalent, localized or delocalized)** between one or more carbon atoms of an organic group or molecule and a main group, transition, lanthanide, or actinide metal atom (or atoms).

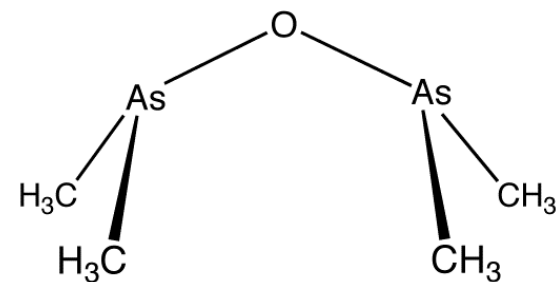
Following longstanding tradition, organic derivatives of the metalloids such as **boron, silicon, germanium, arsenic, and tellurium** also are included in this definition.

It is also understood that the element to which carbon is bound is **more electropositive than carbon** in organometallic chemistry.

*Traditional chemists do not agree for classifying **metal cyanide complexes** as organometallic*

Discovery of Cocodyl

- Cadet was working on cobalt solutions for use as invisible inks. The two common ores of cobalt, smaltite (CoAs_2) and cobaltite (CoAsS_2), both contain arsenic, and arsenic trioxide was formed as a by-product. When he pyrolyzed this oxide with potassium acetate, Cadet got a red-brown liquid that fumed in air and gave off a terrible stench.



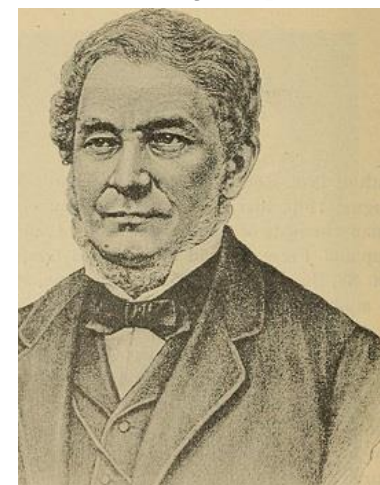
Cacodyl oxide
Discovered in 1760



Cadet de Gassicourt
(1731–1799)

Parisian military apothecary

- Bunsen prepared numerous derivatives of cacodyl, including the cyanide. He nearly died after tasting a cyanide derivative of cocodyl—an experience which no doubt hastened the decline of tasting as a generally practiced analytical technique.
- He lost part of the sight of one eye when a little cacodyl oxide exploded on a heated surface.



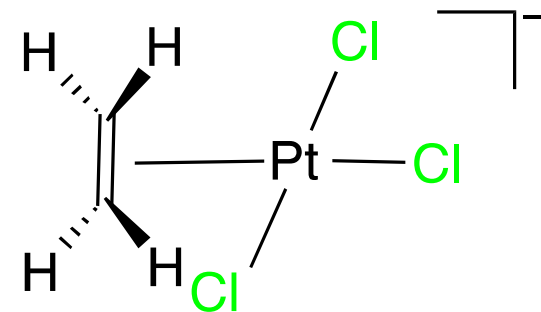
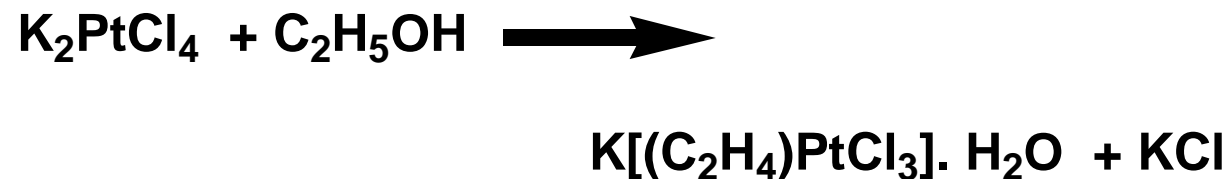
Robert Bunsen
(1811–1899)
German Chemist

Zeise's Salt- The first transition metal organometallic compound



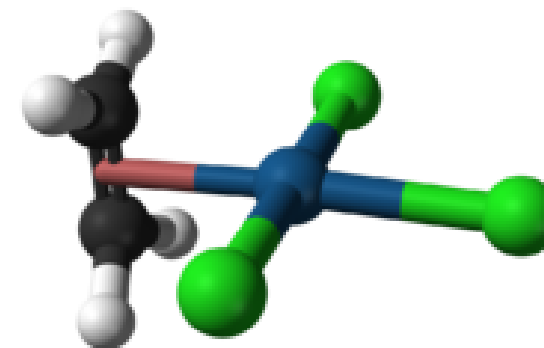
W C Zeise, Danish
pharmacist, **1789-
1847**

*Also father of the
chemistry of
mercaptans R-SH*



Discovery 1827

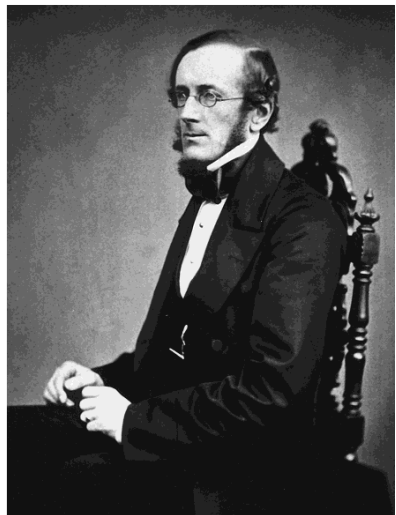
**Structure ~ 150
years later (1975)**



The breakthrough, the isolation of a pure, crystalline compound came when Zeise refluxed K_2PtCl_4 in ethanol and evaporated the resulting solution. Beautiful lemon yellow crystals, often one half inch or more in length were isolated. **The choice of Platinum was fortunate!!**

Chemists in those days often reported how the compounds that they had prepared tasted. Zeise described the taste of this potassium salt as metallic, astringent and long lasting.'

First σ -bonded Organometallic Compound- Diethylzinc

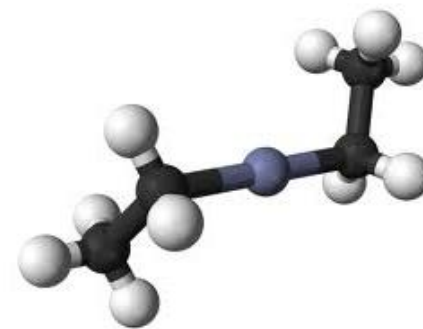


Edward Frankland
1825-1899

Frankland coined
the term
“Organometallic”



Student of Robert Bunsen (Bunsen burner fame!). Prepared diethyl zinc while trying to make ethyl radicals.

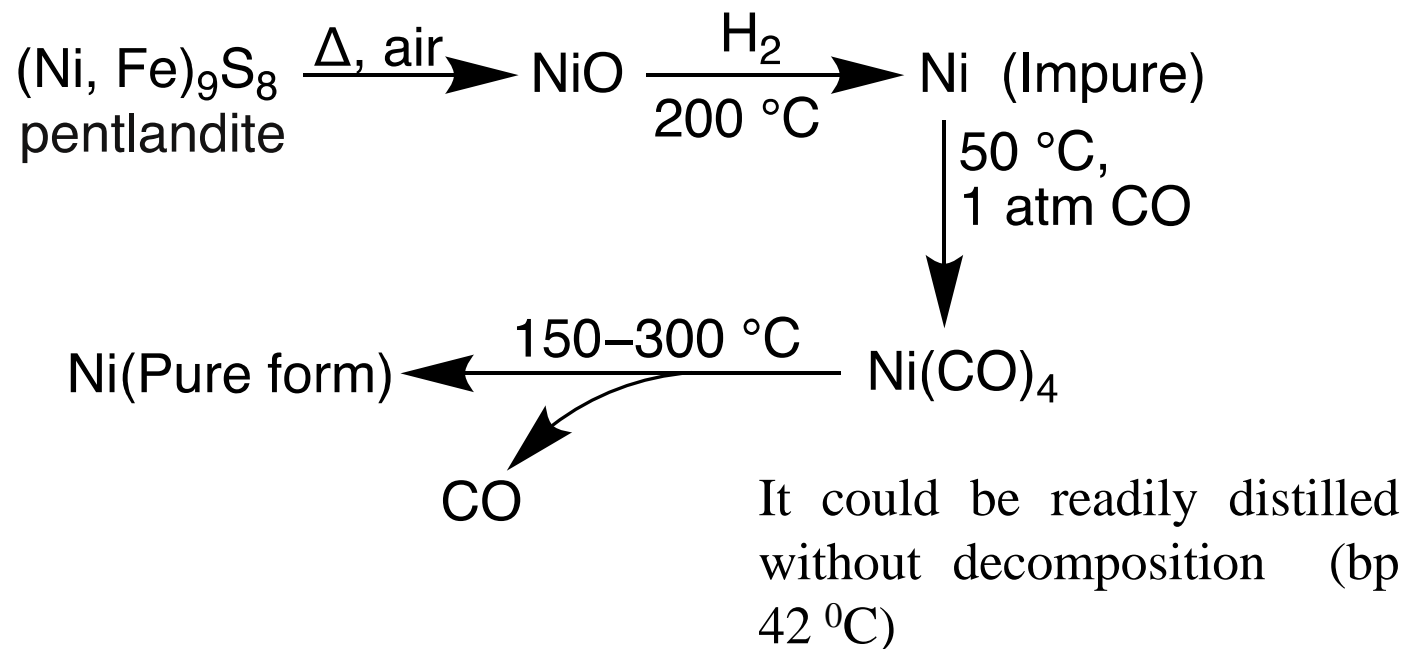


As the early 1850s English chemist Edward Frankland described flasks exploding, throwing bright green flames across his lab, as he heroically distilled dialkylzinc compounds under an atmosphere of **hydrogen**.

Discovery of Nickel Tetracarbonyl

Solvay process. The production of sodium carbonate (Na_2CO_3) using aqueous NaCl , CaCO_3 , and NH_3 had become very important commercially by the later part of 19th century. The reaction vessels contained valves made of nickel, which corroded severely during many of these reactions.

Mond Process for the Purification of Nickel



Ludwig Mond 1839-1909

Father of Metal Carbonyl Chemistry

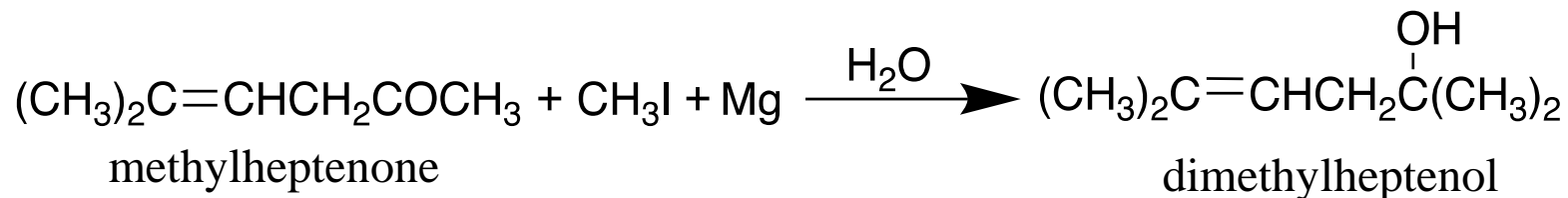
Founder of Imperial Chemical Industry, England

‘Mond nickel company’ was making over 3000 tons of nickel in 1910 with a purity level of 99.9%

The Grignard Reagent



François Auguste Victor Grignard 1871-1935



He was the PhD student of Philippe Barbier. He discovered the Grignard reaction in 1900. He became a professor at the University of Nancy in 1910 and was awarded the Nobel Prize in Chemistry in 1912.

