Modern Coordination Chem

19th Century

① Alfred Werner (Swiss) 1866 - 1919
② Sofus Mads Jørgenson (Danish) 1837 - 1914 } organic chemists by training

Werner was Jørgenson Student

offered fundamentally different pictures of how TM complexes were structured.

Werner won the Nobel Prize in 1913

① Platinum Metal Rev. 1992, 36, 217
② The British Journal on the History of Science 1997, 30, 203
③ J. Chem. Ed. 1959, 36, 521

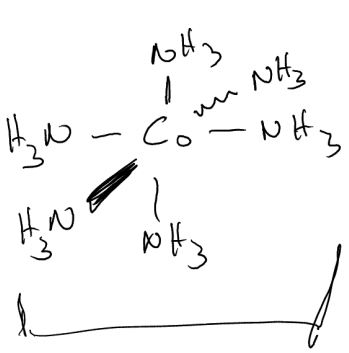
} Jørgenson contributions.

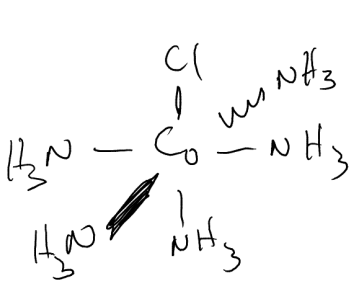
Made + Studied the following

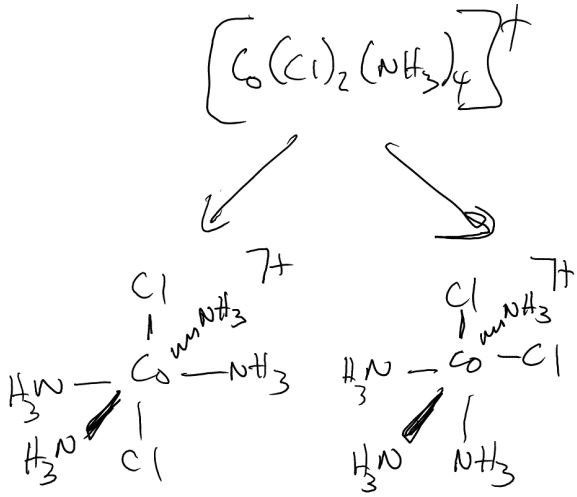
$CoCl_3 + NH_3 \longrightarrow$ Array of Products

$CoCl_3 \cdot 6NH_3$ (Yellow) $\xrightarrow{Ag^{\oplus}}$ 3 AgCl
$CoCl_3 \cdot 5NH_3$ (Purple) $\longrightarrow$ 2 AgCl
$CoCl_3 \cdot 4NH_3$ (Green) $\longrightarrow$ 1 AgCl
$CoCl_3 \cdot 4NH_3$ (violet) $\longrightarrow$ 1 AgCl

} Six coordinate metal complexes are common.







Electronic Structure of TM Complexes

① Valence Bond Theory – Pauling
↳ Not in favor today

② Crystal Field Theory (CFT) – Bethe + Van Vleck
↳ Model that shows how the symmetry of an electrostatic field perturb TM orbital energy levels
↳ Highly symmetry based

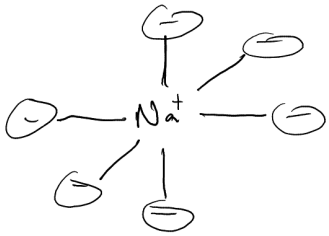
③ Ligand Field Theory – Griffith + Orgel
↳ LFT ⇒ Roots in CFT + builds in an MO perspective

④ Angular Overlap Method
↳ Highly computational, builds on LFT + takes into account the energetics of individual M-L bonding interactions

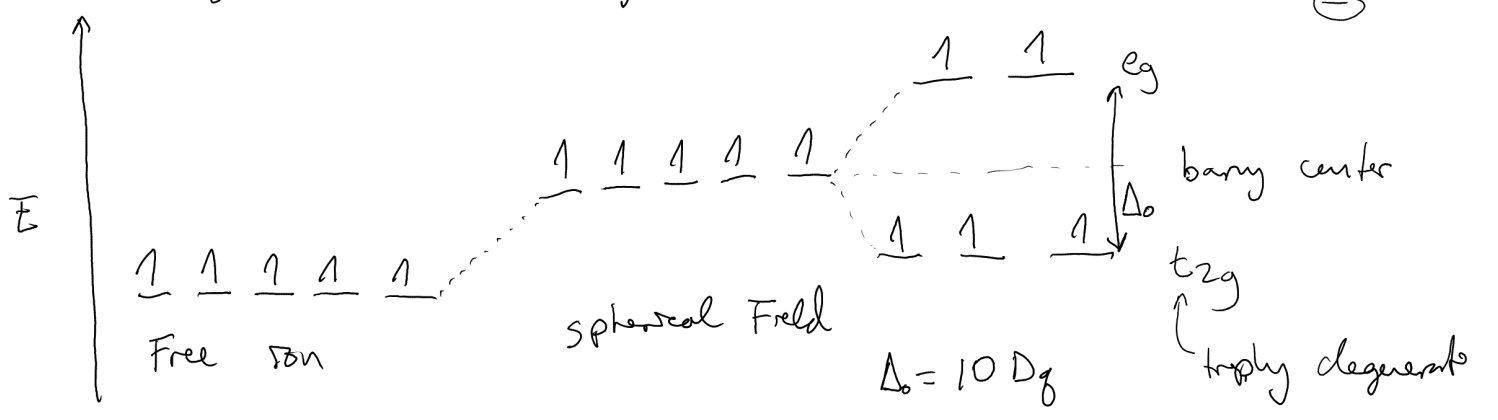
CFT – describe the energy of metal ions within a crystalline lattice.
↳ oxide + halide (Na^+ into a NaCl)

Orbitals on the metal are split or perturbed by the electrostatic field created by the anions in the lattice
↳ Symmetry / position of anions within lattice will have a strong influence on splitting

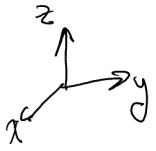
Crystal Field ⇒ Electrostatic Field



d^5 metal ion (Fe^{3+})



dz^2 is a linear combination



z^2-x^2

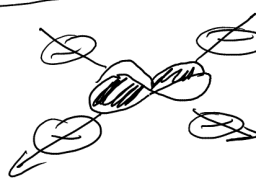
z^2-y^2

$\Rightarrow 2z^2-x^2-y^2$

z^2

dz^2

Eg



dx^2-y^2

O_h ($m3m$)	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$ ($=C_4^2$)	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2,\ \sqrt{3}\,(x^2-y^2))$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

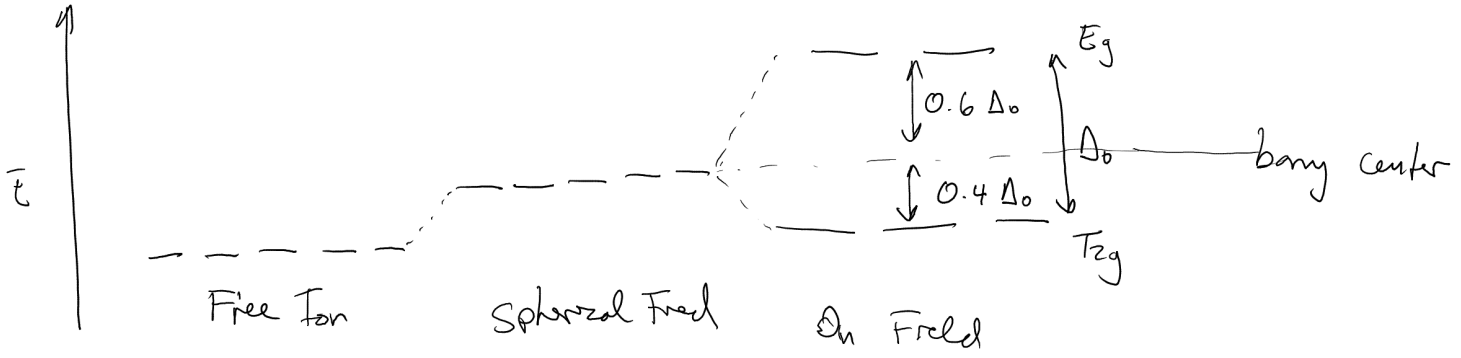
s orbital

d orbital

T_d ($\bar{4}3m$)	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	−1	−1		
E	2	−1	2	0	0		$(2z^2-x^2-y^2,\ \sqrt{3}\,(x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z)	z^2
T_2	3	0	−1	−1	1	(x, y, z)	(xy, xz, yz)

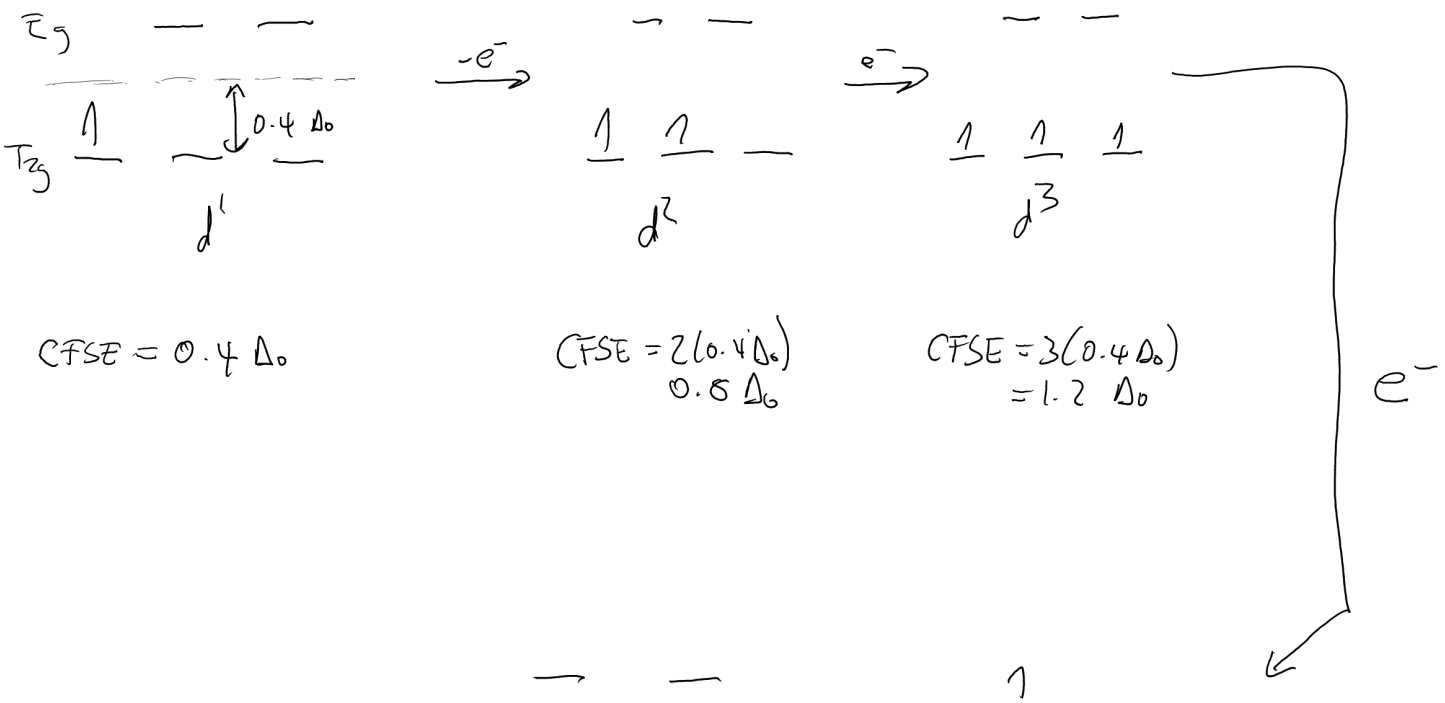
1 of 3 T_{2g}

dxy

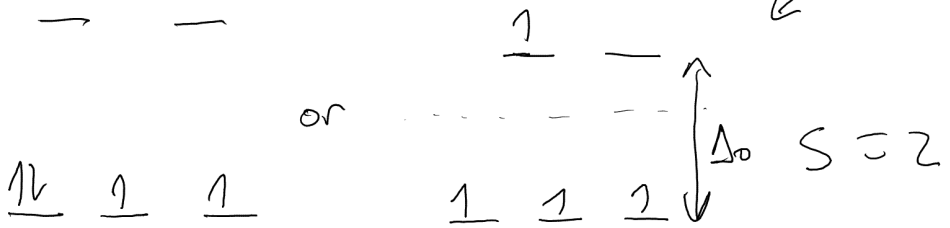


$2(0.6) - 3(0.4) = 0$

$[NbCl_6]^{2-}$ $Nb^{IV}: d^1$ B. E. Borsten Inorg. Chem 1986, 25, 837



P = Pairing Energy



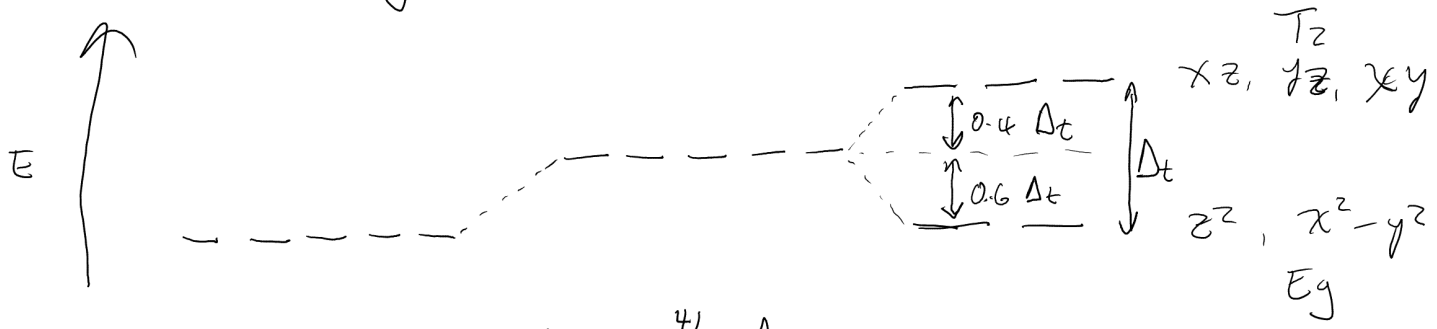
S = 1

CFSE = 4(0.4 Δo) − P = 1.6 Δo − P

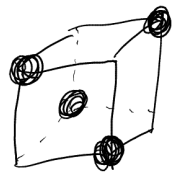
CFSE = 3(0.4 Δo) − 0.6 Δo = 0.6 Δo

Depending on Magnitude of Δo HS or LS Electron Configs are possible

Tetrahedral Crystal Field

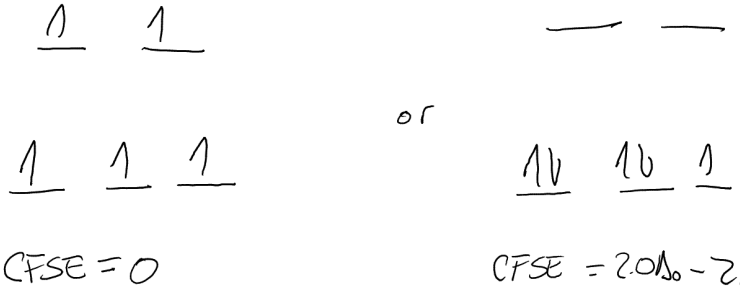


$\Delta t = {}^{4}/_{9}\,\Delta_o$



Co^{III} d^5

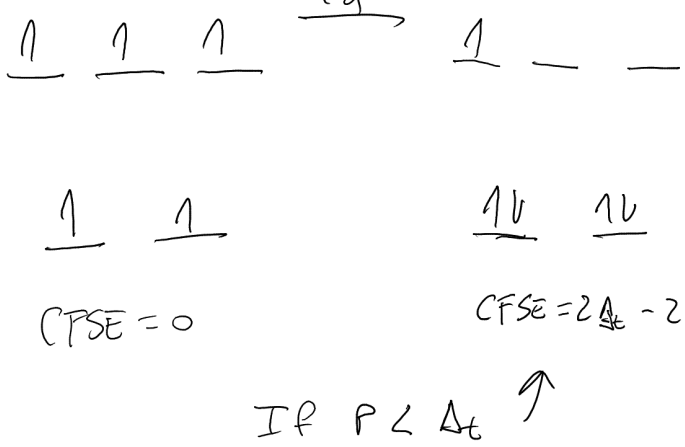
O_h



LS Td Complexes are exceedingly Rare...

$Me^{\ominus}$ strong field ligand

$[Co^{III}(norbornyl)_4]$ LS doublet + Td geometry.



Chem. Comm. 1986, 1491-92

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