Coordination Chemistry

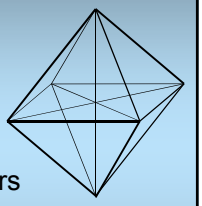
1890's: $CoCl_2 \cdot 6H_2O + NH_3/NH_4^+$

S.M.Jørgensen
1837-1914

Reacted with	Name (colour)	Formula
H_2O_2 + act. charcoal	Luteocobalt chloride	$[Co(NH_3)_6]Cl_3$
H_2O_2 (only)	Purpureocobalt chloride	$[Co(NH_3)_5Cl]Cl_2$
Air, evapo-rate with HCl	Praseocobalt chloride	trans-$[Co(NH_3)_4Cl_2]Cl$
Heating the green trans	Violeocobalt chloride	cis-$[Co(NH_3)_4Cl_2]Cl$

Coordination number 6

Octahedral geometry



- Cobalt(III) ion in centre
- Donor atoms (N, Cl) in corners

Very common geometry in coordination compounds

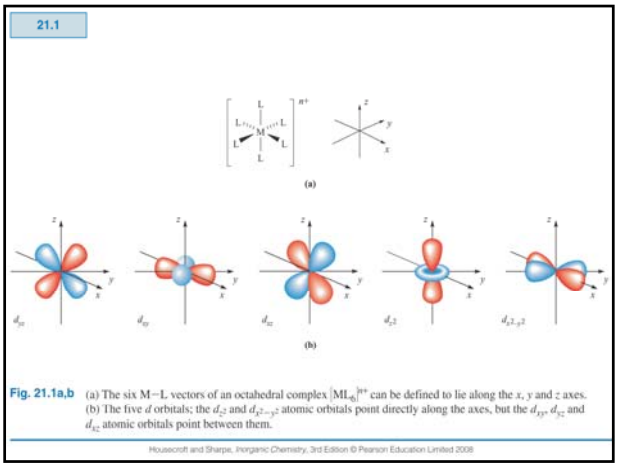


Fig. 21.1a,b (a) The six M−L vectors of an octahedral complex $[ML_6]^{n+}$ can be defined to lie along the x, y and z axes. (b) The five d orbitals; the d_{z^2} and $d_{x^2-y^2}$ atomic orbitals point directly along the axes, but the d_{xy}, d_{yz} and d_{xz} atomic orbitals point between them.

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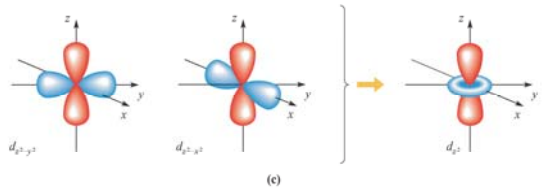
21.2



(c)

Fig. 21.1c (c) The formation of a d_{z^2} orbital from a linear combination of $d_{x^2-y^2}$ and $d_{z^2-x^2}$ orbitals. (Continued)

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21.3

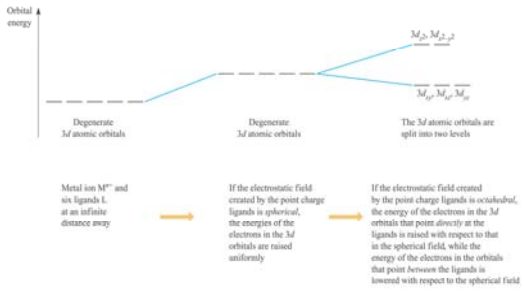

Fig. 21.2 The changes in the energies of the electrons occupying the 3*d* orbitals of a first row M^{n+} ion when the latter is in an octahedral crystal field. The energy changes are shown in terms of the orbital energies. Similar diagrams can be drawn for second (4*d*) and third (5*d*) row metal ions.

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21.1

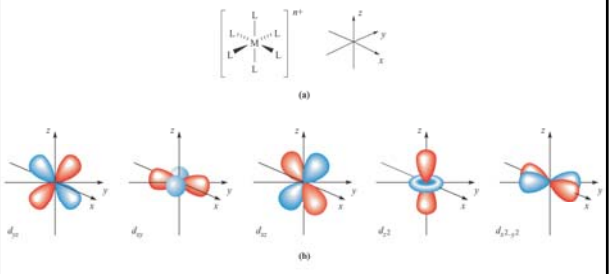

Fig. 21.1a,b (a) The six M−L vectors of an octahedral complex $[ML_6]^{n+}$ can be defined to lie along the *x*, *y* and *z* axes. (b) The five *d* orbitals; the d_{z^2} and $d_{x^2-y^2}$ atomic orbitals point directly along the axes, but the d_{xy}, d_{yz} and d_{xz} atomic orbitals point between them.

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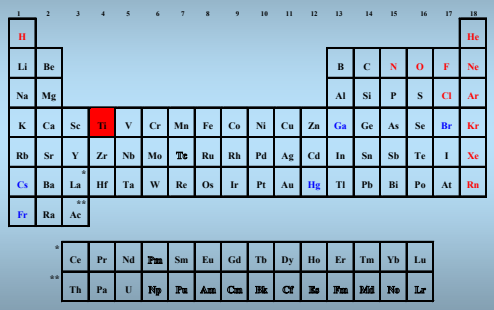
$_{22}$Ti



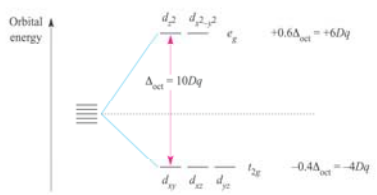
Ti(III)

- Ti: $(1s)^2\,(2s)^2\,(2p)^6\,(3s)^2\,(3p)^6\,(4s)^2\,(3d)^2$
- Ti: $[Ar]\,(4s)^2\,(3d)^2$

- Ti(III) : $[Ar]\,(3d)^1$ i.e. a single d-electron
- Ti(III) : a d^1 – system

- Octahedral coordination compounds e.g. $Ti(H_2O)_6^{3+}$ in strong acid

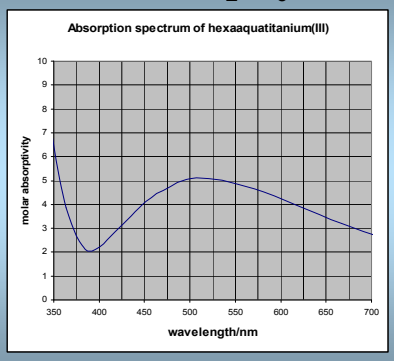
21.4



How does that relate to experiment?

Fig. 21.3 Splitting of the *d* orbitals in an octahedral crystal field, with the energy changes measured with respect to the barycentre, the energy level shown by the hashed line.

$Ti(H_2O)_6^{3+}$ in acid



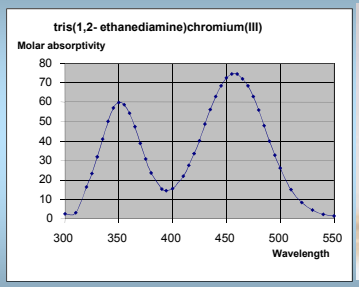
Molar absorptivity ε in $(M \cdot cm)^{-1}$ of Lambert-Beers law

$A = \varepsilon \cdot C \cdot \ell$

$(\lambda, \varepsilon)_{max} = (508, 5.1)$

Absorption spectrum

aqueous solution



$(\lambda, \varepsilon)_{max}$ = (457 , 75.0), (351 , 60.5) og $(\lambda, \varepsilon)_{min}$ = (394 , 14.5).

First absorption band for *trans*-$Co(NH_3)_4X_2^{n+}$

**cis-isomer in this case*

Notes table 1 p.25

X	NO_2^-	NH_3	H_2O	* ½ ox^{2-}	* ½ CO_3^{2-}	Cl^-
$\lambda_{max.1}$/nm	442	474	500	510	524	600
σ_1 /$10^3 cm^{-1}$	22.62	21.1	20.00	19.61	19.06	16.67

The spectrochemical series

- Blueshift of absorption maxima resulting from the ligand independent of metal ion:

I^-, Br^-, S^{2-}, Cl^-, N_3^-, OH^-, $C_2O_4^{2-}$, H_2O, NCS, ,py, NH_3, en, phen, NO_2^-, CH_3^-, $C_6H_5^-$, CN^-, CO

First absorption band for $Co(NH_3)_5X^{m+}$

Notes table 2 p.21

X	NO_2^-	NH_3	ONO^-	H_2O	NCS^-	NO_3^-	SO_3^{2-}	OH^-	ox^{2-}	CO_3^{2-}	$S_2O_4^{2-}$	Cl^-	Br^-
$\lambda_{max.1}$ /nm	455	474	472	487	498	498	500	502	507	508	515	530	542
σ_1/ 10^3cm^{-1}	21.98	21.1	21.19	20.5	20.08	20.08	20.0	19.9	19.72	19.69	19.42	18.87	18.42

First absorption band for MX_6^{p+}

Notes table 3&4 p.21

	CN^-	½en	½bipy	½phen	NH_3	ONO^-	NCS^-	½ox^{2-}	H_2O
λ M= Co		464	455	457	474	484	565	602	606
λ M= Cr	376	457	466	473	465			572	575

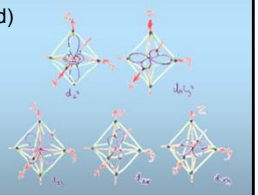
Colour: energy difference

— — $d_{z^2}, d_{x^2-y^2}$

— — — d_{xy}, d_{yz}, d_{zx}

Repulsive influence from ligand electron pairs (the ligand field) on d-electrons in one energy level

is taken as the sum of the effect of 6 (different ?) ligands.



Average environment rule

- Holoedrised ligand field:

red ligands (on Z-axis) are averaged. Same for ligands on Y-axis and X-axis.

Average environment rule

Colour: $\lambda = (\sigma)^{-1}$

of MA_nB_{6-n}

$$\sigma_{max.1}\left(MA_nB_{6-n}\right) = \frac{n}{6}\cdot\sigma_{max.1}\left(MA_6\right) + \frac{6-n}{6}\cdot\sigma_{max.1}\left(MB_6\right)$$

Average environment rule

- Calculation in the $Crox_nen_{3-n}^{(3-2n)-}$

n	λ_{max1}(obs)/nm	σ_{max1}(obs)/kcm^{-1}	σ_{max1}(calc)/kcm^{-1}	λ_{max1}(calc)/nm
3	572	17.48	-	-
2	530	18.87	18.95	528
1	495	20.22	20.43	489
0	457	21.90	-	-

Variation through metals

Different Δ-values for different metal ions

Variation of Δ_{oct} down a group with the same ligand

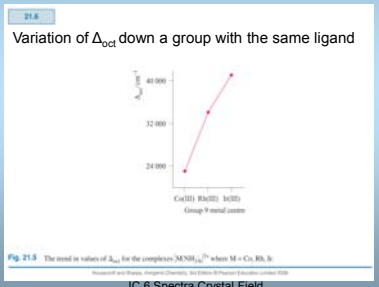


Fig. 21.5 The trend in values of Δ_{oct} for the complexes $[MNH_3]^{3+}$ where M = Co, Rh, Ir.