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1. **Orgel Diagram,**
2. Selection Rule for electronic transitions,
3. Calculation of Dq, B and β Para

Measurement of UV- Visible spectrum

1. Solution Spectra : OD vs wavelength, ε Vs wavelength

2. DRS Spectra

Preparation of solution : Prepare 10^{-3} to 10^{-4} M solution of metal complexes in suitable solvent .

Selection solvent

- Solvent should not absorb ultraviolet radiation in the same region as the substance whose spectrum is being determined.
- Usually solvents which do not contain conjugated systems .
- Solvent should be transparent .
- , Water, EtOH, Acetone, DMSO, DMF , THF , N- Hexane, Dichloromethane
- We also Know the λ_{max} of Solvent , it is useful during interpretation.
- We should know the expected absorption bands in the spectrum.

To avoid doubt , note down the spectrum of :

1.Spectrum of metal salt which is taken for synthesis of complex

2. Spectrum of Ligand which is taken for synthesis of complex

3. Spectrum of synthesized metal complex .

4. Observe the intensity of bands, sharpness and broadness of bands

5. Before interpretation we should know , either complex is high spin or Low spin

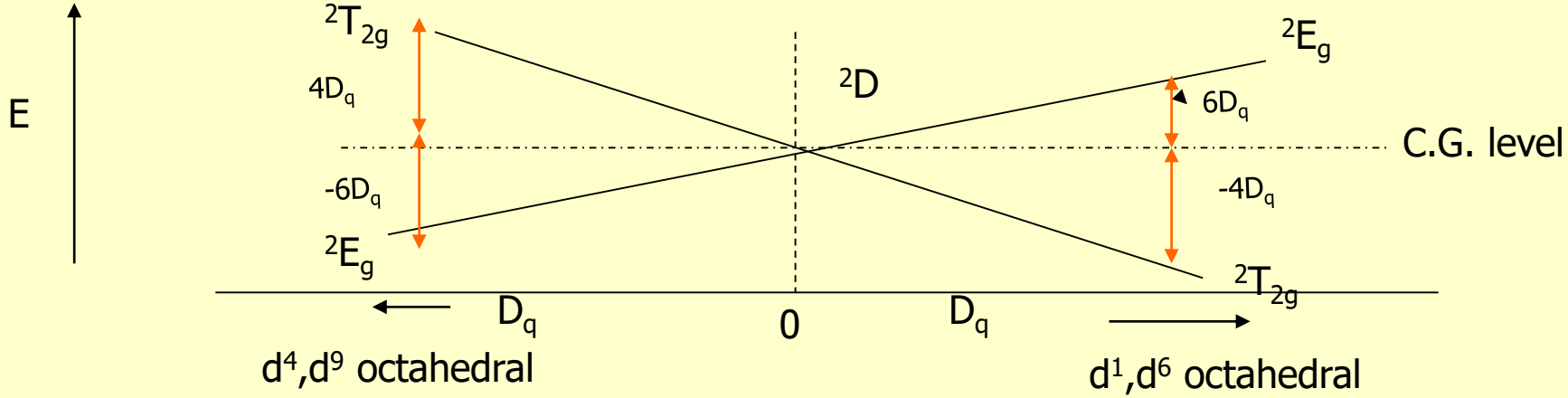
Orgel diagram for octahedral complexes:

- Ligand field theory was first applied by L. E. Orgel for the interpretation of spectroscopic properties of transition metal complexes. Its diagram is applicable for high spin type complexes.

Construction :

- Using energy of ground state term and magnitude of ligand field strength.
- Non- crossing rule is applicable at the time of construction of diagram.
- Parent spin multiplicity should be given to the crystal field terms.

Orgel diagram for d^1,d^9,$d^4$and d^6 configuration for an octahedral complexes.



The diagram of **d^n (O_h) reverse $d^{(10-n)}$ (O_h)**

Type of electronic transition can be represented

$d^1 = {}^2D = {}^2T_{2g} \longrightarrow {}^2E_g$

Ex . : Ti^{+3},

$d^9 = {}^2D = {}^2Eg \longrightarrow {}^2T_{2g}$

Ex . : Cu^{+2},

d^n (Oh) Reverse to $d^{(10-n)}$ (Oh)

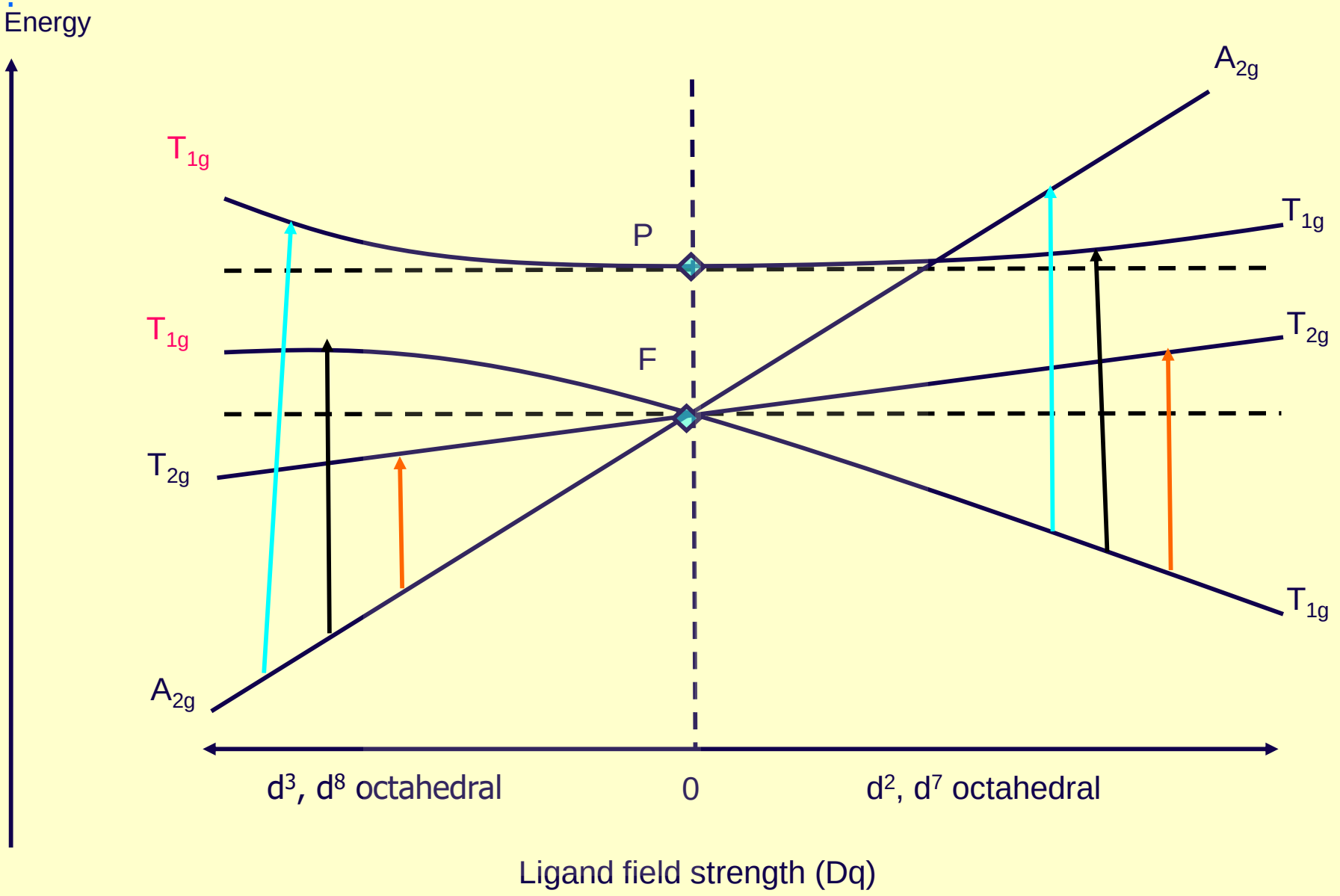
$d^6 = {}^5D = {}^5T_{2g} \longrightarrow {}^5E_g$

Ex . : Co^{+3}, Rh^{+3}

$d^4 = {}^5D = {}^5Eg \longrightarrow {}^5T_{2g}$

Ex . : Cu^{+2},

Orgel diagram for d^2,d^8, d^3 and d^7 configuration for an octahedral complexes:



Following types of transitions are expected

For d^2 Configuration

$^3T_{1g} \rightarrow {}^3T_{2g}$

$^3T_{1g} \rightarrow {}^3A_{2g}$

$^3T_{1g} \rightarrow {}^3T_{1g}$

For d^8 Configuration

$^3A_{2g} \rightarrow {}^3T_{1g}$

$^3A_{2g} \rightarrow {}^3T_{2g}$

$^3A_{2g} \rightarrow {}^3T_{1g}$

For d^3 Configuration

$^4T_{1g} \rightarrow {}^4T_{2g}$

$^4T_{1g} \rightarrow {}^4A_{2g}$

$^4T_{1g} \rightarrow {}^4T_{1g}$

For d^7 Configuration

$^4A_{2g} \rightarrow {}^4T_{1g}$

$^4A_{2g} \rightarrow {}^4T_{2g}$

$^4A_{2g} \rightarrow {}^4T_{1g}$

Selection Rule for electronic transitions:

Spin selection rule ; $\Delta S=0$ - Spin allowed transition

There must be no change in spin multiplicity during an electronic transition

Singlet – singlet, Triplet- Triplet, -- -- Spin allowed transition --- strong band , broad
doublet- doublet

$^3T_{1g} \longrightarrow {}^3T_{2g}$ Spin allowed transitions

Spin forbidden transition – violet selection rule $\Delta S \neq 0$

Singlet – triplet, Triplet- doublet -- Spin forbidden transition - weak band

Laporte Selection Rule = $\Delta l = \pm 1$

There must be a change in parity during an electronic transition

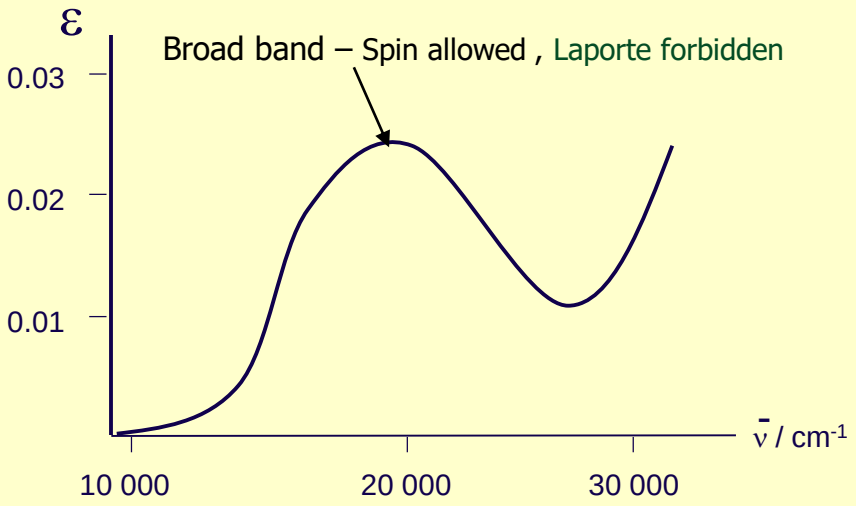
g ←→ u Laporte's allowed
p ←→ d

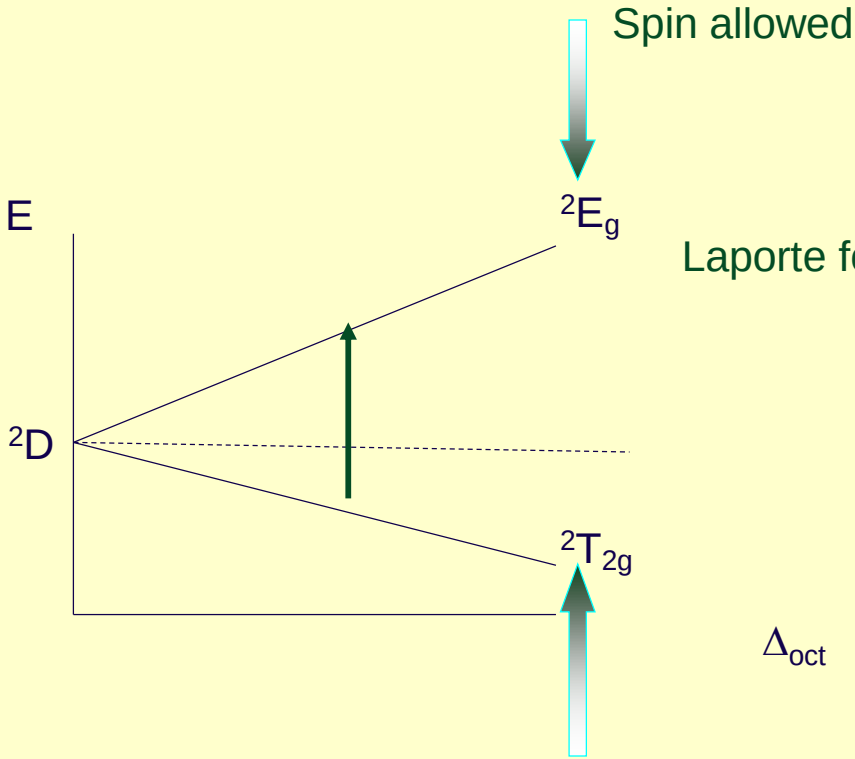
g ←→ g Laporte's forbidden
u←→ u Laporte's forbidden

Selection rules determine the intensity of electronic transitions

Selection rules determine the intensity of electronic transitions and shape of band

$[Ti(OH_2)_6]^{3+}$, d^1, O_h field





Selection Rules and molar extinction coefficient ;

Transition	ε	complexes
Spin forbidden Laporte forbidden	$10^{-3} – 1$	Many d^5 O_h COMP. $[Mn(OH_2)_6]^{2+}$
Spin allowed Laporte forbidden	1 – 10	Many O_h COMP. $[Ni(OH_2)_6]^{2+}$
	10 – 100	Some square planar $[PdCl_4]^{2-}$
	100 – 1000	6-coordinate complexes of low symmetry, and square planar with organic ligands
Spin allowed Laporte allowed	$10^2 – 10^3$	Some MLCT bands in comp. with unsaturated ligands
	$10^3 – 10^6$	Many CT bands, transitions in organic species

Centro-symmetric – Less intense band – trans isomer of complexes

Calculation of Dq, B and β Parameter ; Konig's Method ;

Applicable for d^2,d^3,d^7 & d^8 configurations in an octahedral complexes.
A) d^3 and d^8 configuration in an octahedral complexes.

$\nu_1 = E[{}^4A_{2g} \longrightarrow {}^4T_{2g}] = 10\ D_q$

$\nu_2\ E[{}^4A_{2g} \longrightarrow {}^4T_{1g}] = 0.5\{[15B+30Dq-0.5\{[15B-10Dq]^2+120DqB]\}^{0.5}$

$\nu_3 = E[{}^4A_{2g} \longrightarrow {}^4T_{1g}] = 0.5\{[15B+30Dq+ 0.5\{[15B-10Dq]^2+120DqB]\}^{0.5}$

1) If ν_1 **&** ν_2 **observed** $B_{(comp)} = (2\nu_1^2 + \nu_2^2 - 3\ \nu_1\nu_2)/(15\nu_2 - 27\nu_1)$

2) If ν_1 **,** ν_2 **&** ν_3 **observed** $B_{(comp} = (\nu_2 + \nu_3 - 3\ \nu_1)/15B)$

$\beta = B_{(comp)}/B_{(free\ ion)}$

Problem : Absorption spectra of $[CrF_6]^{3-}$ ion gives three bands with a peaks at 14900, 22700 and 34400 cm^{-1} . Calculate, D_q, B and β parameters and assign the types of transitions [Given : $B_{(free\ ion)}$ =918 cm^{-1}]

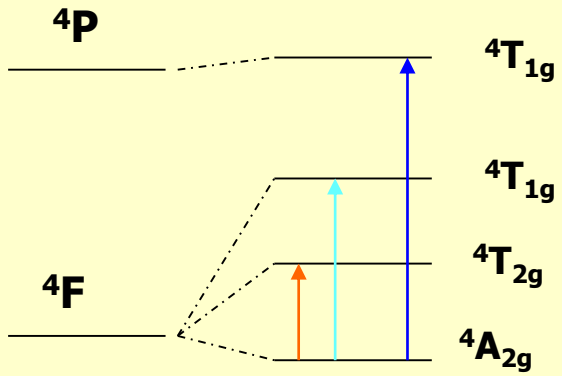
Cr = $3d^5 4s^1$,

In the given $[CrF6]^{3-}$ ion chromium is under Cr^{3+}

Cr(III) = $3d^3$ = ^4F = $^4A_{2g}$ +$^4T_{2g}$ +$^4T_{1g}$

^4P = $^4T_{1g}$

The complex has given three bands



ν_1= 14900, ν_2= 22700, ν_3= 34400 cm-1

10Dq = ν_1= 14900

Dq = 1490 cm^{-1}

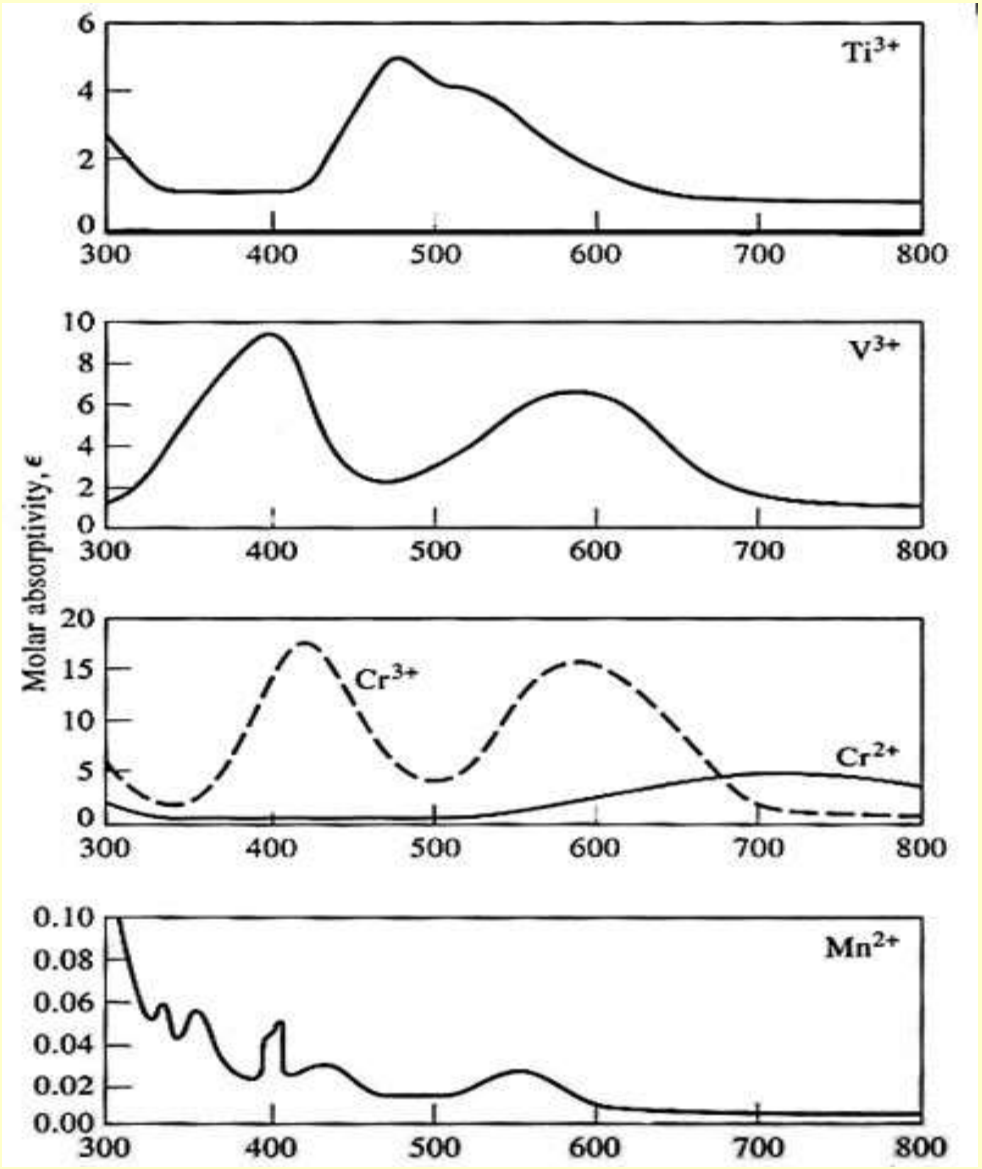
$\mathbf{B_{(complex)} = (}\nu_2 + \nu_3 - 3\ \nu_1)/\ 15$

= (22700 + 34400 -3 x14900)/ 15

= 826.67 cm^{-1}

β = $\mathbf{B_{(complex)}}$/ $B_{(free\ ion)}$

826.67/918 = 0.901


Molar absorptivity, ε
Ti3+
V3+
Cr3+
Cr2+
Mn2+
300
400
500
600
700
800

Questions :

48.Fill in the blanks of the following

Name of the complex ion	Configuration	Absorption band (cm^{-1})	Dq	Type of transition
$[TiCl_6]^{3-}$		13000		
$[TiF_6]^{3-}$		18900		
$[Ti(CN)_6]^{3-}$		22300		
$[Cu(H_2O)_6]^{2+}$		12000		
$[Fe(H_2O)_6]^{2+}$		10400		
$[Fe(CN)_6]^{4-}$		32200		
$[Fe(CNO)_6]^{4-}$		27000		
$[Co(CN)_6]^{-3}$		26100		
$[Co(H_2O)_6]^{3+}$		20760		
$Cr(H_2O)_6]^{2+}$		14100		

THE END