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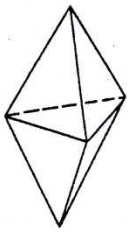
Table I-10.7 Polyhedral symbols (*continued*)

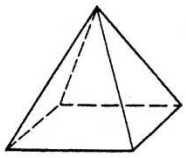
Polyhedra of five-coordination

trigonal bipyramid



TBPY-5

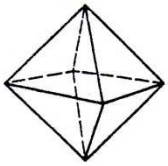
square pyramid



SPY-5

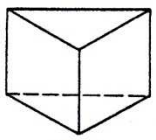
Polyhedra of six-coordination

octahedron



OC-6

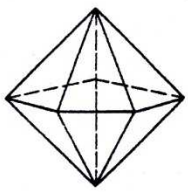
trigonal prism



TPR-6

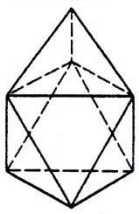
Polyhedra of seven-coordination

pentagonal bipyramid



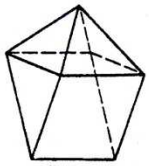
PBPY-7

octahedron, face monocapped



OCF-7

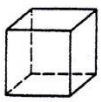
trigonal prism, square face monocapped



TPRS-7

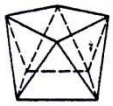
Polyhedra of eight-coordination

cube



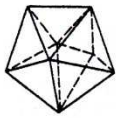
CU-8

square antiprism



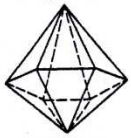
SAPR-8

dodecahedron



DD-8

hexagonal bipyramid



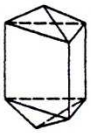
HBPY-8

Polyhedra of eight-coordination

octahedron, trans-bicapped

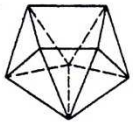
OCT-8

trigonal prism, triangular face bicapped



TPRT-8

trigonal prism, square face bicapped



TPRS-8

Polyhedra of nine-coordination

trigonal prism, square face tricapped

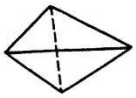
TPRS-9

heptagonal bipyramid

Table I-10.7 Polyhedral symbols and geometrical structures

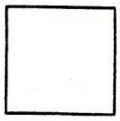
Polyhedra of four-coordination

tetrahedron



T-4

square planar



SP-4

IUPAC
1990, 2005
Nomenclature
of Inorganic
Chemistry

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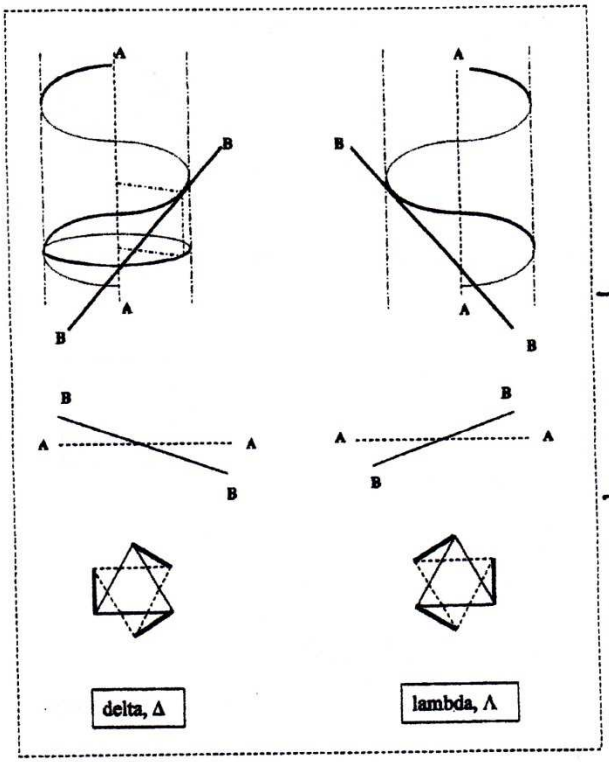
puckered rings

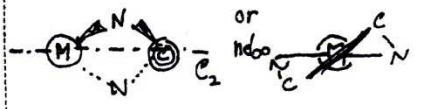
Chiral conformations of chelate rings

Chirální konformace chelátového kruhu – např. 5členný ethylendiamin(en)

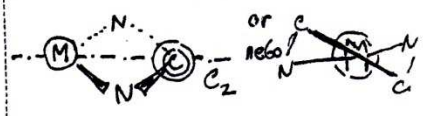
symetrie kruhu: C_2 symmetry



λ



δ



rozdíly mezi diastereoizomery

- řádově 2-3 kJ/mol ΔH
- význam ΔS importace!

energy difference

enantiomorfní páry pro tris(chelátů)

1: $\Lambda(\delta\delta\delta)$ $\Delta(\lambda\lambda\lambda)$

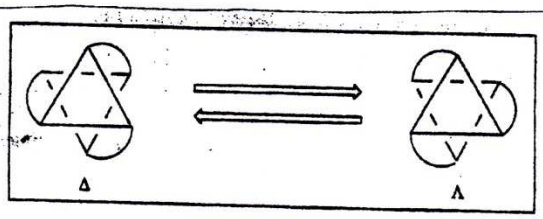
2. $\Lambda(\delta\delta\lambda)$ $\Delta(\lambda\lambda\delta)$

3. $\Lambda(\delta\lambda\lambda)$ $\Delta(\lambda\delta\delta)$

4. $\Lambda(\lambda\lambda\lambda)$ $\Delta(\delta\delta\delta)$

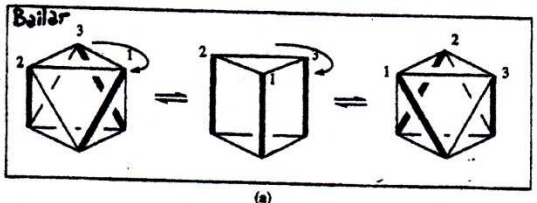
enantiomorphous pairs

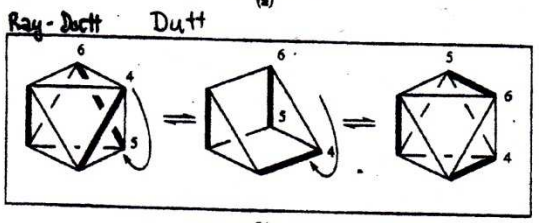
ex: Cotton, Wilkinson, p. 33



racemization

twists





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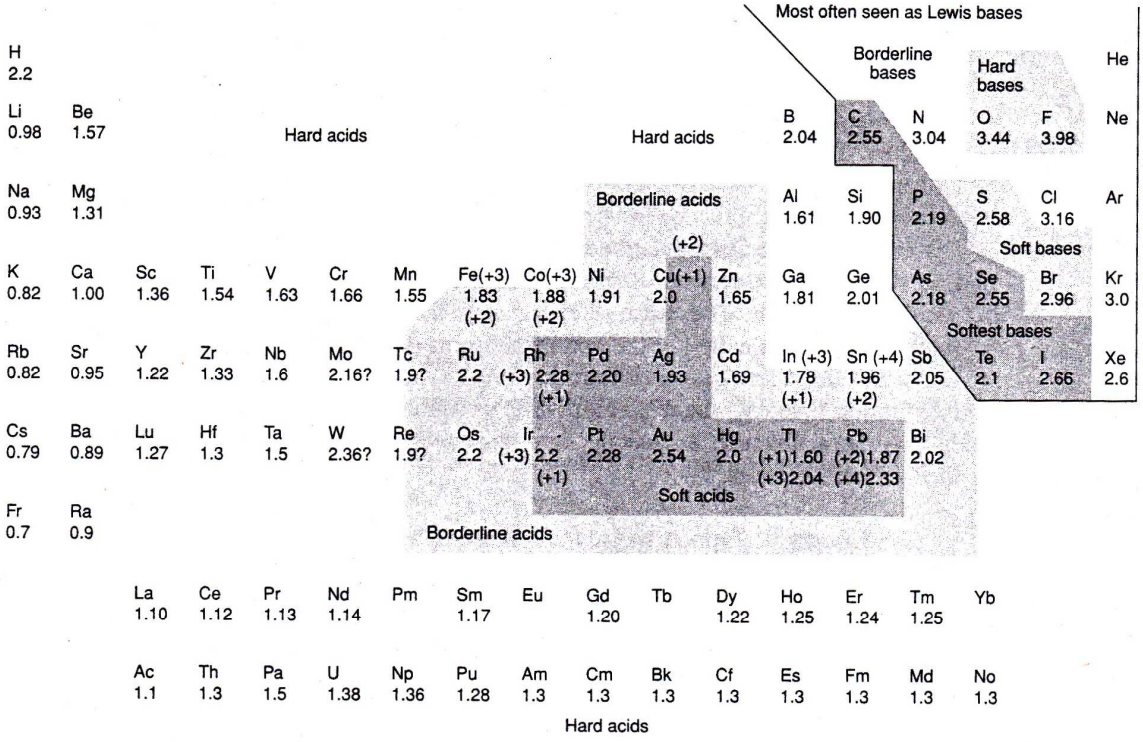
Characteristic properties				
property	hard acids	soft acids	soft bases	hard bases
electronegativity	0,7 – 1,6	1,9 – 2,5	2,1 – 3,0	3,4 – 4,0
ionic radius [pm]	< 90	> 90	> 170	~ 120
charge	≥ +3	≤ +2		

HARD AND SOFT LEWIS ACIDS AND BASES

Wulfsberg, Inorganic Chemistry:

Table 5.1
Hard and Soft Acids and Bases[a]



[a]Numbers in parentheses are oxidation numbers. The number below each atomic symbol is the Pauling electronegativity of that element.

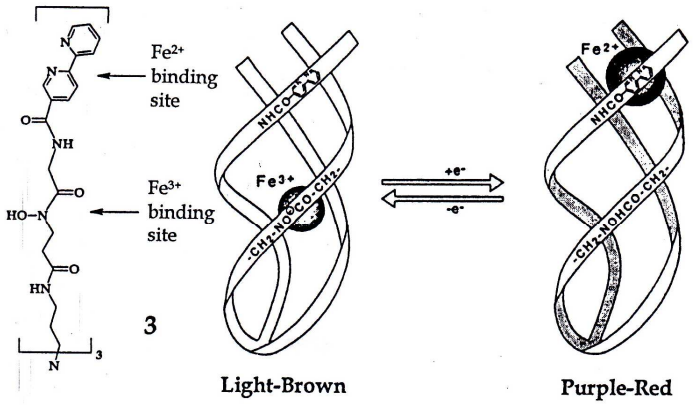


Figure 9.6: Helical structure 2 is capable of translocating iron ions between binding sites based on their redox state.[10] *Reprinted with permission of Nature.*

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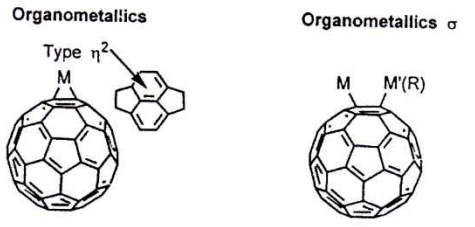


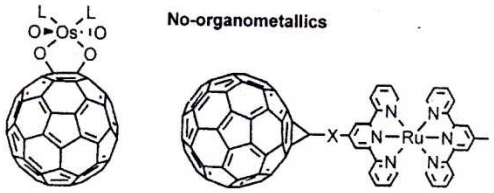
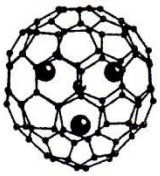


Figure 2.24 Different kinds of metallofullerenes.



endofullerene

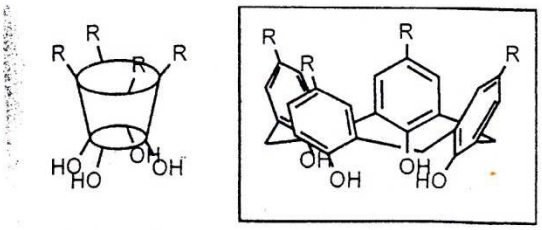
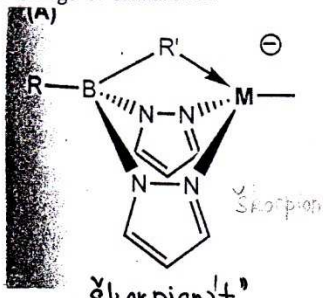
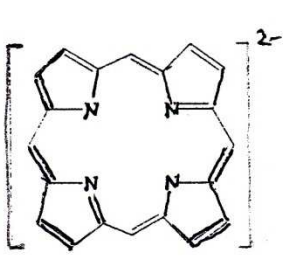


Figure 2.19 Different drawings of calixarenes.



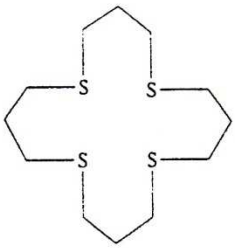
„škorpionát"
scorpionate

Makrocykly Macrocycles

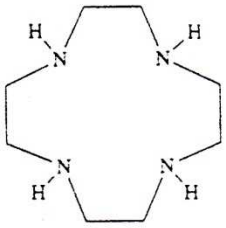


(1-XVI)

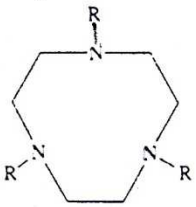
porfyrine



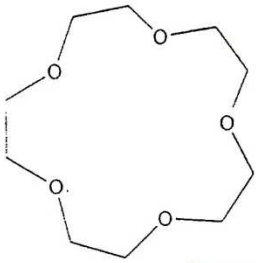
(1-XVII)



(1-XVIII)

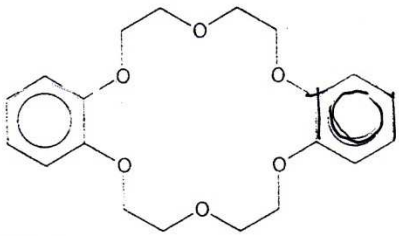


(1-XIX)

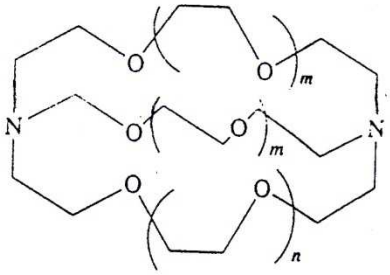


(1-XX)

crown-ethery
„věnčité"

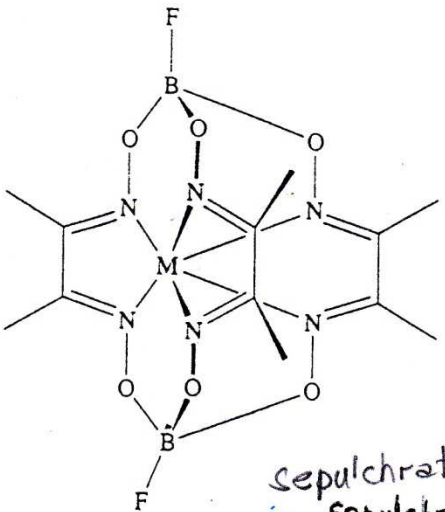


(1-XXI)



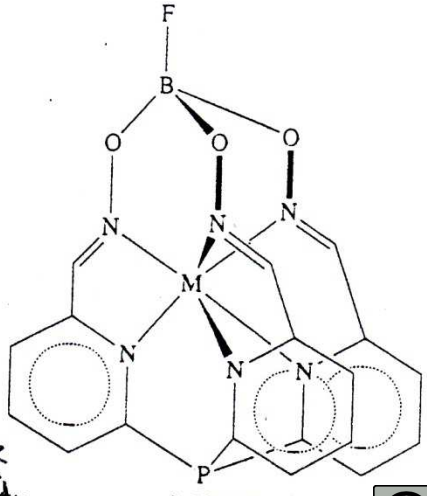
(1-XXII)

kryptand- m,m,n
Cryptand



(1-XXIII)

sepulchrate
sepulchráty



(1-XXIV)

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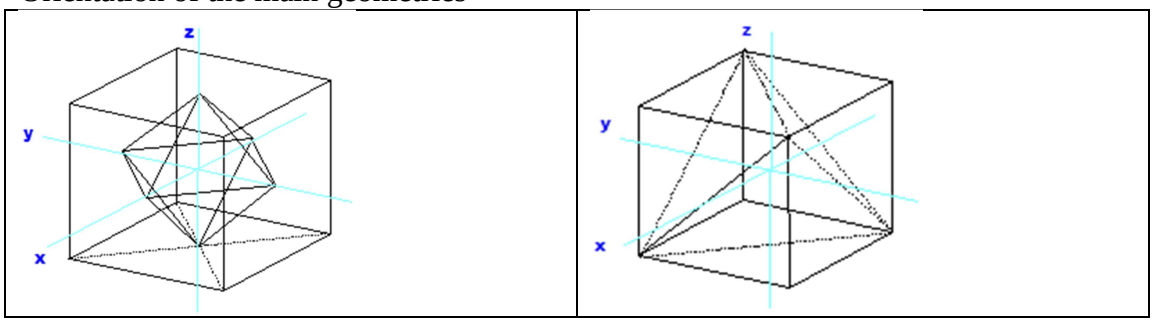
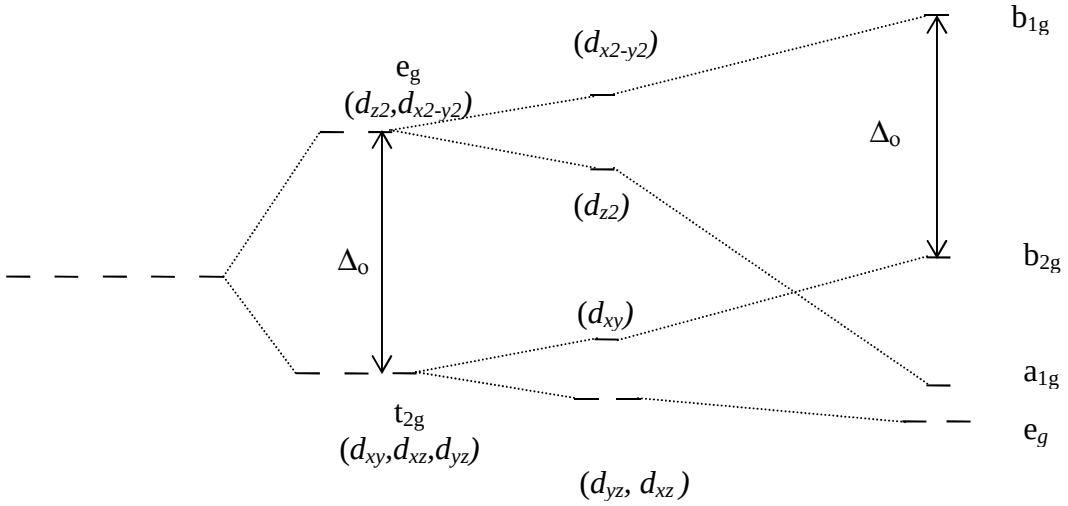
Orientation of the main geometries



Energy Levels of *d* Orbitals in Complexes of Various Geometries[a]

CN[b]	Geometry	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}	Largest Splitting
2	Linear[c]	1.028	−0.628	−0.628	0.114	0.114	0.914
3	Trigonal[d]	−0.321	0.546	0.546	−0.386	−0.386	0.867
4	Tetrahedral	−0.267	−0.267	0.178	0.178	0.178	0.445
4	Square planar[d]	−0.428	1.228	0.228	−0.514	−0.514	1.000
5	Trigonal bipyramid[e]	0.707	−0.082	−0.082	−0.272	−0.272	0.789
5	Square pyramid[e]	0.086	0.914	−0.086	−0.457	−0.457	0.828
6	Octahedron	0.600	0.600	−0.400	−0.400	−0.400	1.000
6	Trigonal prism	0.096	−0.584	−0.584	0.536	0.536	0.680
7	Pentagonal bipyramid[e]	0.493	0.282	0.282	−0.528	−0.528	0.810
8	Cube	−0.534	−0.534	0.356	0.356	0.356	0.890
8	Square antiprism	−0.534	−0.089	−0.089	0.356	0.356	0.445
9	Tricapped trigonal prism	−0.225	−0.038	−0.038	0.151	0.151	0.189
12	Icosahedron	0.000	0.000	0.000	0.000	0.000	0.000

[a] Units of Δ_o, the octahedral crystal field splitting, assuming the same overall charge density and distance. [Adapted from J. E. Huheey, E. A. Keiter, and R. L. Keiter, *Inorganic Chemistry: Principles of Structure and Reactivity*, 4th ed., Harper-Collins, New York, 1993, p. 405.]
[b] Coordination number = CN.
[c] Ligands lie along *z* axis.
[d] Ligands lie in *xy* plane.
[e] Pyramid base in *xy* plane.



degenerated *d* orbitals	octahedron	tetragonal bipyramid, elongated, *z*-axis	square

TABLE 4.2

Octahedral Crystal Field Splitting Energies Δ_o, cm^{-1}

$(M')^{2+}$	$(M')^{3+}$	$(M'')^{3+}$	$(M''')^{3+}$
	Cr^{2+}, Cr^{3+}, Mo^{3+}		
$[CrCl_6]^{4-}$ 13,000	$[CrCl_6]^{3-}$ 13,200	$[MoCl_6]^{3-}$ 19,200	
$[Cr(H_2O)_6]^{2+}$ 14,000	$[Cr(H_2O)_6]^{3+}$ 17,400		
	$[Cr(NH_3)_6]^{3+}$ 21,500		
$[Cr(en)_3]^{2+}$ 18,000	$[Cr(en)_3]^{3+}$ 21,900		
	$[Cr(CN)_6]^{3-}$ 26,600		
	Co^{2+}, Co^{3+}, Rh^{3+}, Ir^{3+}		
		$[RhCl_6]^{3-}$ 20,000	$[IrCl_6]^{3-}$ 25,000
$[Co(H_2O)_6]^{2+}$ 9,300	$[Co(H_2O)_6]^{3+}$ 18,200	$[Rh(H_2O)_6]^{3+}$ 27,000	
$[Co(NH_3)_6]^{2+}$ 10,100	$[Co(NH_3)_6]^{3+}$ 22,900	$[Rh(NH_3)_6]^{3+}$ 34,100	$[Ir(NH_3)_6]^{3+}$ 41,000
$[Co(en)_3]^{2+}$ 11,000	$[Co(en)_3]^{3+}$ 23,200	$[Rh(en)_3]^{3+}$ 34,600	$[Ir(en)_3]^{3+}$ 41,400
	$[Co(CN)_6]^{3-}$ 33,500	$[Rh(CN)_6]^{3-}$ 45,500	
	Mn^{2+}, Mn^{3+}		
$[MnCl_6]^{4-}$ 7,500	$[MnCl_6]^{3-}$ 20,000		
$[Mn(H_2O)_6]^{2+}$ 8,500	$[Mn(H_2O)_6]^{3+}$ 21,000		
$[Mn(en)_3]^{2+}$ 10,100			
	Fe^{2+}, Fe^{3+}		
	$[FeCl_6]^{3-}$ 11,000		
$[Fe(H_2O)_6]^{2+}$ 8,500	$[Fe(H_2O)_6]^{3+}$ 14,300		
$[Fe(CN)_6]^{4-}$ 32,800	$[Fe(CN)_6]^{3-}$ 35,000		

Changes in Crystal Field Stabilization Energies[a]

			CFSE ML_6 (oct)	**CFSE ML_5 (sp)**	**ΔCFSE**	
d^1			0.40	0.46	+0.06	
d^2			0.80	0.91	+0.11	
d^3			1.20	1.00	−0.20	
	Low-spin–strong field			**High-spin–weak field**		
	CFSE ML_6 (oct)	**CFSE ML_5 (sp)**	**ΔCFSE**	**CFSE ML_6 (oct)**	**CFSE ML_5 (sp)**	**ΔCFSE**
d^4	$1.60 - P$	$1.46 - P$	−0.14	0.60	0.91	+0.31
d^5	$2.00 - 2P$	$1.91 - 2P$	−0.09	0	0	0
d^6	$2.40 - 2P$	$2.00 - 2P$	−0.40	0.40	0.46	+0.06
d^7	$1.80 - P$	$1.91 - P$	+0.11	0.80	0.91	+0.11
			CFSE ML_6 (oct)	**CFSE ML_5 (sp)**	**ΔCFSE**	
d^8			1.20	1.00	−0.20	
d^9			0.60	0.91	+0.31	
d^{10}			0	0	0	

[a]The CFSEs (in units of Δ_o) for octahedral (oct) and square pyramidal (sp) fields are shown followed by the change in CFSE for the process ML_6 (octahedral) ⟶ ML_5 (square pyramidal). A + indicates a gain in CFSE during the process, and a − indicates a loss in CFSE.

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Mulliken symmetry symbols

Mulliken Symbol	Interpretation
a	Non-degenerate orbital; symmetric to principal C_n
b	Non-degenerate orbital; unsymmetric to principal C_n
e	Doubly degenerate orbital
t	Triply degenerate orbital
(subscript) g	Symmetric with respect to center of inversion *i*
(subscript) u	Unsymmetric with respect to center of inversion *i*
(subscript) 1	Symmetric with respect to C_2 perpendicular to principal C_n
(subscript) 2	Unsymmetric with respect to C_2 perpendicular to principal C_n
(superscript) '	Symmetric with respect to s_h
(superscript) ''	Unsymmetric with respect to s_h

Table 1.3 Splitting of the orbitals in T_d, D_{4h}, D_3 and D_{2d} symmetry fields.

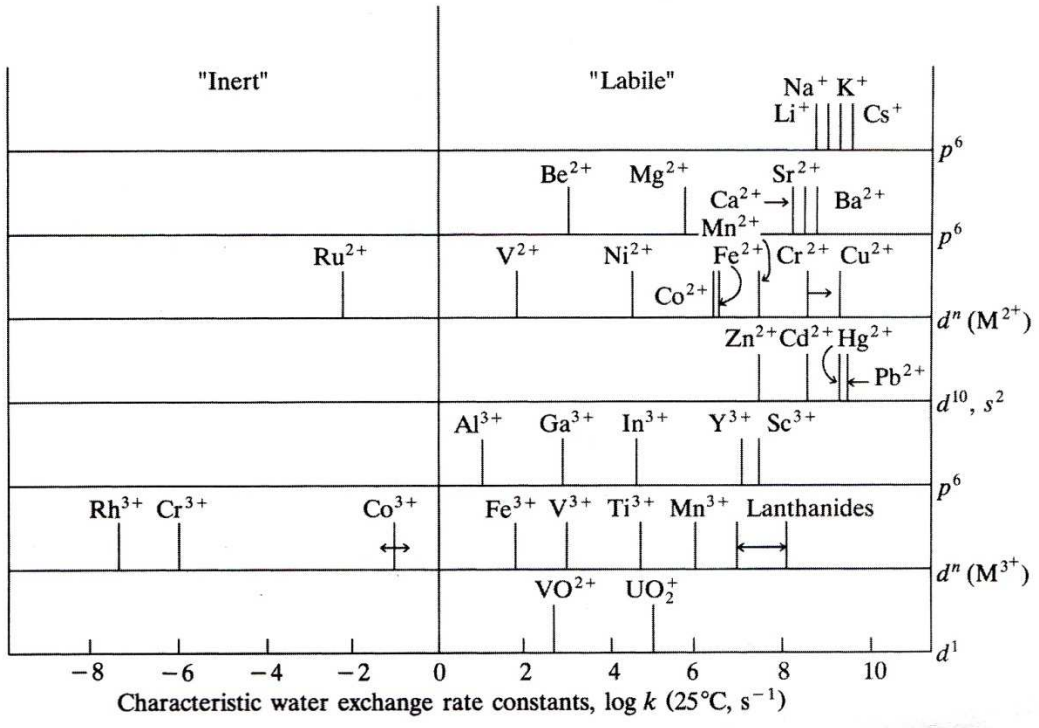
	T_d	D_{4h}	D_3	D_{2d}
s	a_1	a_{1g}	a_1	a_1
p	t_2	$a_{2u} + e_u$	$a_2 + e$	$b_2 + e$
d	$t_2 + e$	$a_{1g} + b_{1g} + b_{2g} + e_g$	$a_1 + 2e$	$a_1 + b_1 + b_2 + e$
f	$a_2 + t_2 + t_1$	$a_{2u} + b_{1u} + b_{2u} + 2e_u$	$a_1 + 2a_2 + 2e$	$a_1 + a_2 + b_2 + 2e$

FIGURE 5.5

Rate constants for water exchange for various ions:

$[M(H_2O)_6]^{m+} + H_2O^{18} \xrightarrow{k} [M(H_2O)_5(H_2O^{18})]^{m+} + H_2O$

Data are tabulated as the log of the rate constant at 25°C. Inert hydrated ions, those that only slowly exchange water molecules between the hydration sphere and bulk water structure, are given on the left, and labile hydrated ions are on the right. (Ref. 7.)



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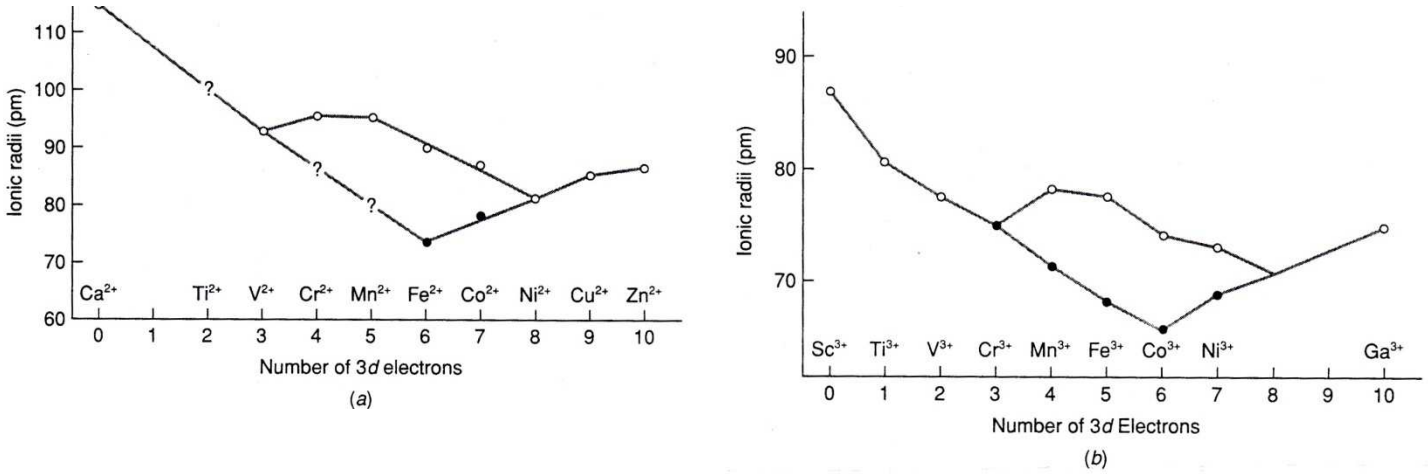

Radii of the +2 ions (*a*) and the +3 ions (*b*) as a function of the $3d^n$ electron configuration. Open circles represent high-spin (weak-field) ions; closed circles represent low-spin (strong-field) ions. [Adapted from R. D. Shannon and C. T. Prewitt, *Acta Crystallogr. Sect. B*, **26**, 1076 (1970).]

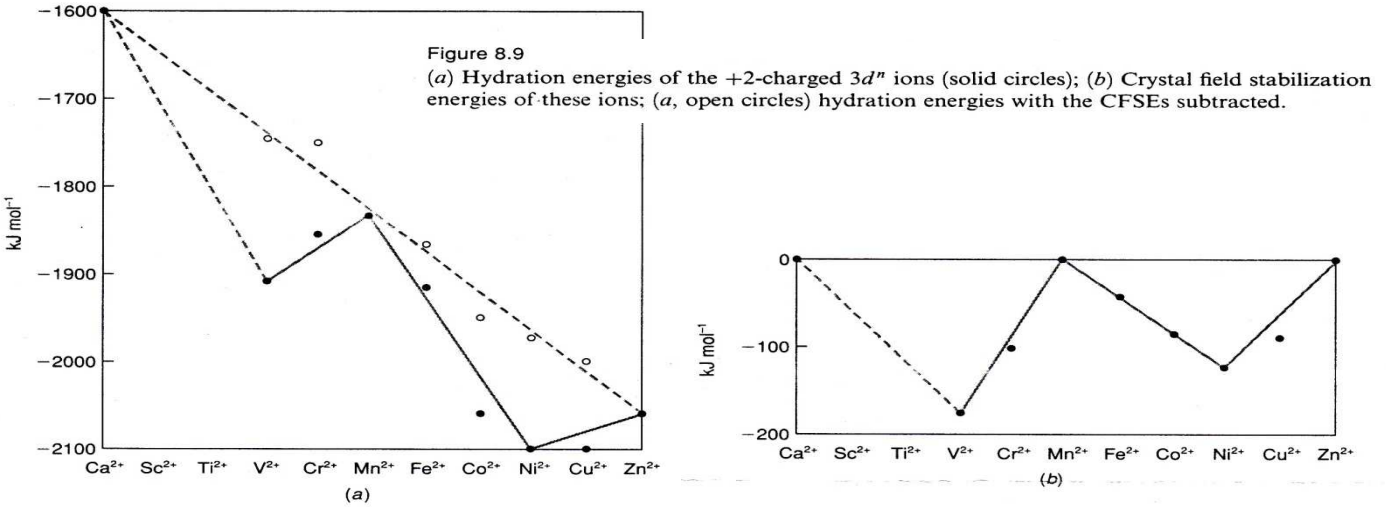

Figure 8.9
(*a*) Hydration energies of the +2-charged $3d^n$ ions (solid circles); (*b*) Crystal field stabilization energies of these ions; (*a*, open circles) hydration energies with the CFSEs subtracted.

Irving – Williams series

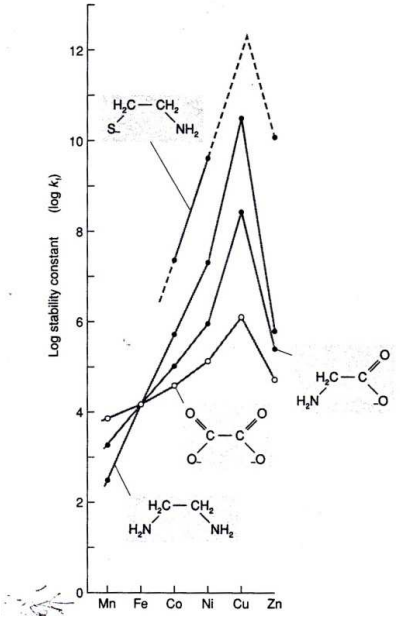

Figure 8.11
Logarithms of stability constants for a given ligand (shown next to each curve) versus the +2-charged metal ion forming the complex. [Adapted from H. Sigen and D. B. McCormick, *Acc. Chem. Res.*, **3**, 201 (1970).]

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Table 17.1
Letters Used in Atomic Term Symbols

Letter	*S*	*P*	*D*	*F*	*G*	*H*	*I*	*K*
Value of *L*	0	1	2	3	4	5	6	7
Degeneracy of *L*	1	3	5	7	9	11	13	15

Table 17.2A
Multiple Terms of Various Electronic Configurations

s^2, p^6, and d^{10}	^1S
p and p^5	^2P
p^2 and p^4	$^3P, ^1D, ^1S$
p^3	$^4S, ^2D, ^2P$
d and d^9	^2D
d^2 and d^8	$^3F, ^3P, ^1G, ^1D, ^1S$
d^3 and d^7	$^4F, ^4P, ^2H, ^2G, ^2F, ^2D, ^2D, ^2P$
d^4 and d^6	$^5D, ^3H, ^3G, ^3F, ^3F, ^3D, ^3P, ^3P, ^1I, ^1G, ^1G, ^1F, ^1D, ^1D, ^1S, ^1S$
d^5	$^6S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G, ^2G, ^2F, ^2F, ^2D, ^2D, ^2D, ^2P, ^2S$

SOURCE: From J. C. Davis, Jr., *Advanced Physical Chemistry: Molecules, Structure, and Spectra*, 1965, The Ronald Press Co., New York.

$$N = \frac{(2y)!}{x!(2y-x)!}$$

N – the total number of ways that *x* electrons can be placed in *y* orbitals of equivalent energy with either of two different spins = number of microstates

Table 17.2B
The Splitting of Atomic Electronic States in Complexes of O_h Symmetry

Atomic term	Number of states	Terms in O_h symmetry
S	1	A_{1g}
P	3	T_{1g}
D	5	$T_{2g} + E_g$
F	7	$T_{1g} + T_{2g} + A_{2g}$
G	9	$A_{1g} + E_g + T_{1g} + T_{2g}$
H	11	$E_g + T_{1g} + T_{1g} + T_{2g}$
I	13	$A_{1g} + A_{2g} + E_g + T_{1g} + T_{2g} + T_{2g}$

Table 17.3
Arrangement of Microstates for p^2 Electron Configuration According to Their Total Spins and Angular Momenta

Total spin M_S[a]	1	0	−1
$M_L = 2$		1(↑↓)0( )−1( )	
$M_L = 1$	1(↑)0(↑)−1( )	1(↑)0(↓)−1( ) 1(↓)0(↑)−1( )	1(↓)0(↓)−1( )
$M_L = 0$	1(↑)0( )−1(↑)	1( )0(↑↓)−1( ) 1(↑)0( )−1(↓) 1(↓)0( )−1(↑)	1(↓)0( )−1(↓)
$M_L = -1$	1( )0(↑)−1(↑)	1( )0(↑)−1(↓) 1( )0(↓)−1(↑)	1( )0(↓)−1(↓)
$M_L = -2$		1( )0( )−1(↑↓)	

[a] Total spin M_S = sum of spins ($+\frac{1}{2}$ or $-\frac{1}{2}$) of individual electrons.

Ex: G. Wulfsberg, Inorganic Chemistry, University Science Books, 2000

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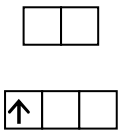
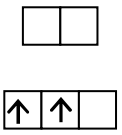
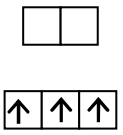
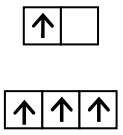
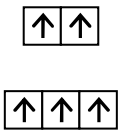
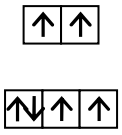
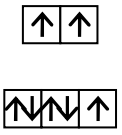
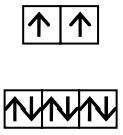
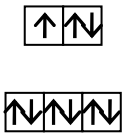
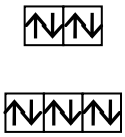
GROUND STATE TERMS IN OCTAHEDRAL SYMMETRY

Weak field = high-spin arrangement

				
$d^1 = {}^2T_{2g}$	$d^2 = {}^3T_{1g}$	$d^3 = {}^4A_{2g}$	$d^4 = {}^5E_g$	$d^5 = {}^6A_{1g}$
				
$d^6 = {}^5T_{2g}$	$d^7 = {}^4T_{1g}$	$d^8 = {}^3A_{2g}$	$d^9 = {}^2E_g$	$d^{10} = {}^1A_{1g}$

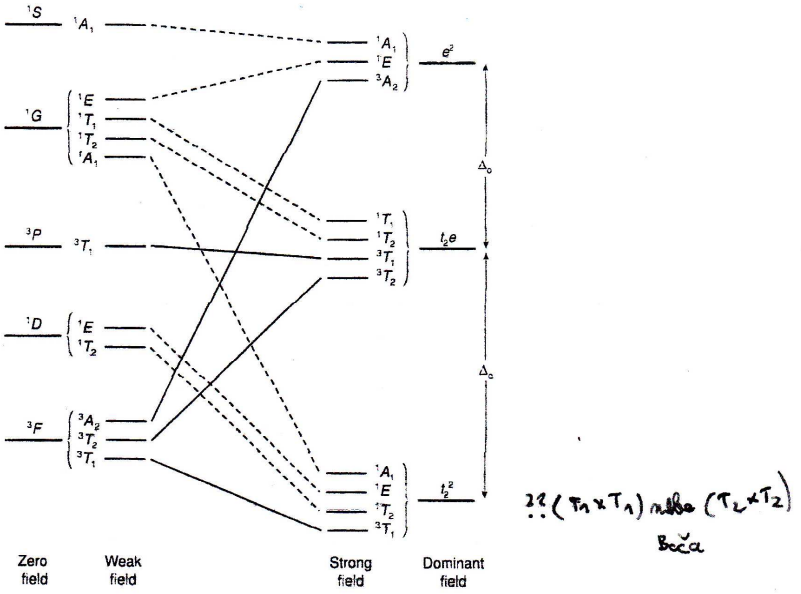
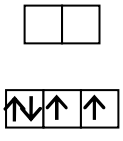
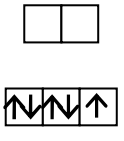
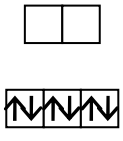
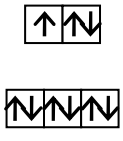


Figure 17.2
Energy levels of a d^2 ion in an octahedral complex as the strength of the ligand field is varied. (Since all energy levels are *gerade*, the "*g*" has been omitted.) [Adapted from F. A. Cotton, G. Wilkinson, and P. L. Gaus, *Basic Inorganic Chemistry*, 3rd ed., John Wiley & Sons, Inc., New York, 1995; p. 527.]

Ex: G. Wulfsberg, Inorganic Chemistry, University Science Books, 2000

Strong field – low-spin arrangement

			
$d^4 = {}^3T_{1g}$	$d^5 = {}^2T_{2g}$	$d^6 = {}^1A_{1g}$	$d^7 = {}^2E_g$