CAPVT VI

KOMPLEKSI

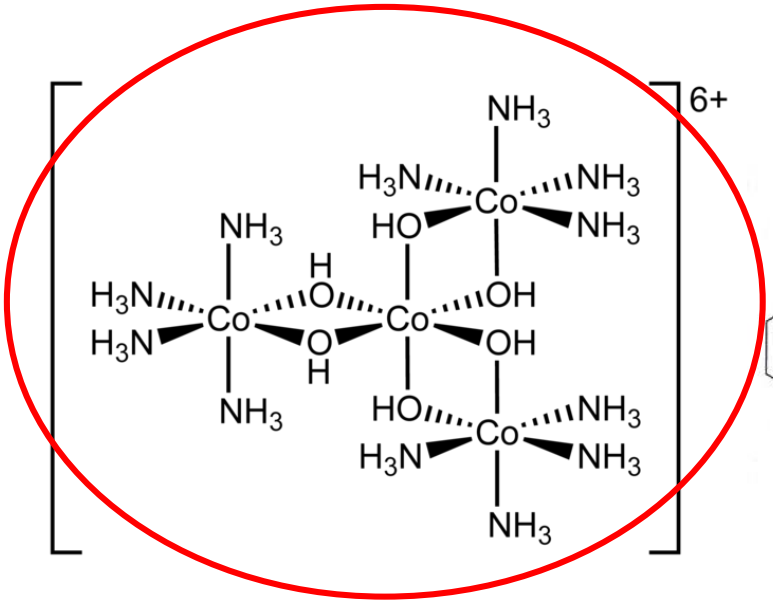
Što je kompleks?

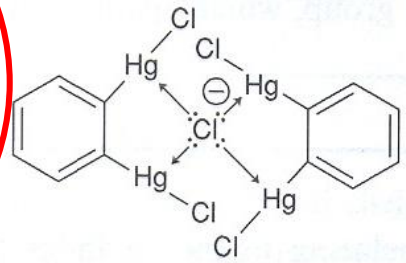
A molecular entity formed by loose association involving two or more component molecular entities (ionic or uncharged), or the corresponding chemical species. The bonding between the components is normally weaker than in a covalent bond. The term has also been used with a variety of shades of meaning in different contexts: it is therefore best avoided when a more explicit alternative is applicable. In inorganic chemistry the term 'coordination entity' is recommended instead of 'complex'.

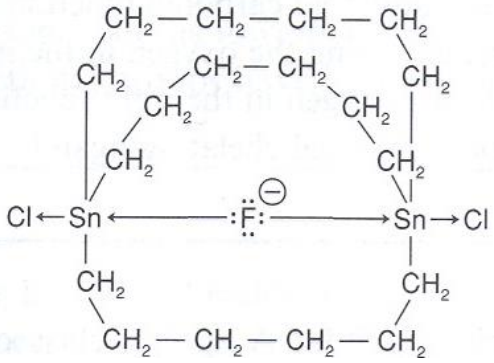
IUPAC

Spoj kiseline i baze

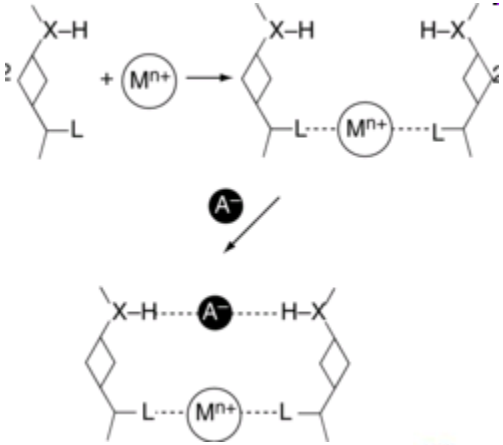
JA



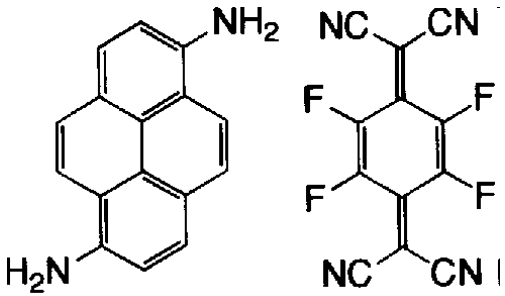




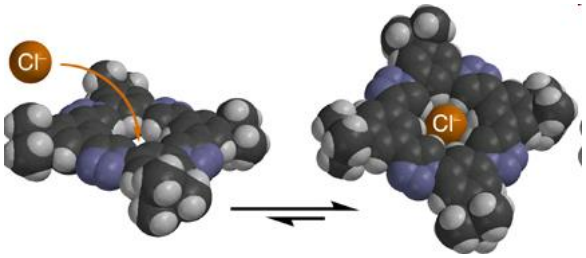
Lewisove



Brønstedove



DAP F4TCNQ



Usanovičeve

Koordinacijski spojevi

- Centralni atom – Lewisova kiselina
- Ligandi – Lewisove baze
  - Monodentatni, polidantatni, ambidentatni, premoščujući, kelatirajući

Koordinacijski spojevi

- Stabilnost
  - Termodinamička, kinetička inertnost
- Boja
- Magnetska svojstva

Stabilnost (*konstanta stabilnosti*)

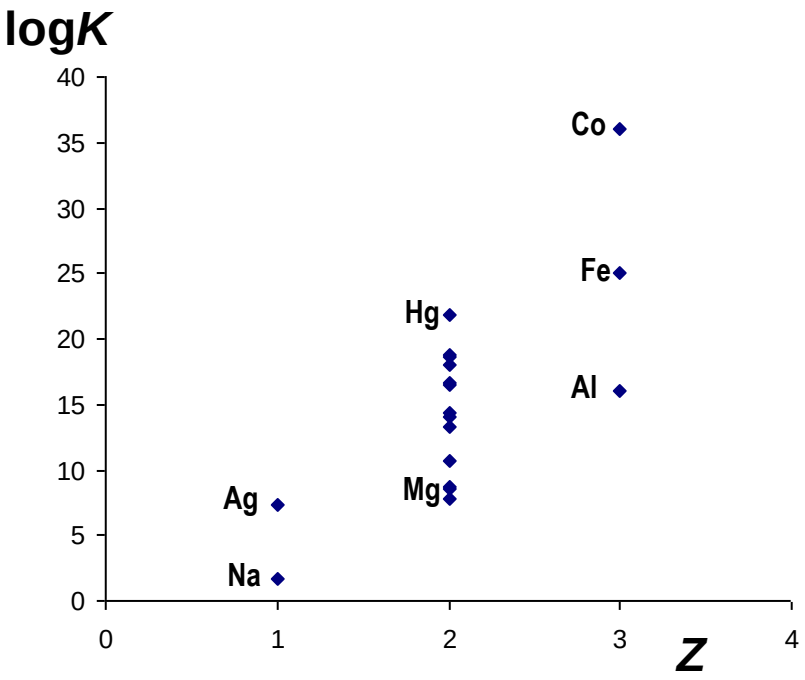
- Ovisi o kationu i ligandu
  - Za isti ligand raste s Z^*/r (za atome pseudoplemenitoplinovske konfiguracije)
    - Irving–Williamsov niz stabilnost kompleksâ za dani ligand dvovalentnog metala prve prijelazne serije raste do bakra →

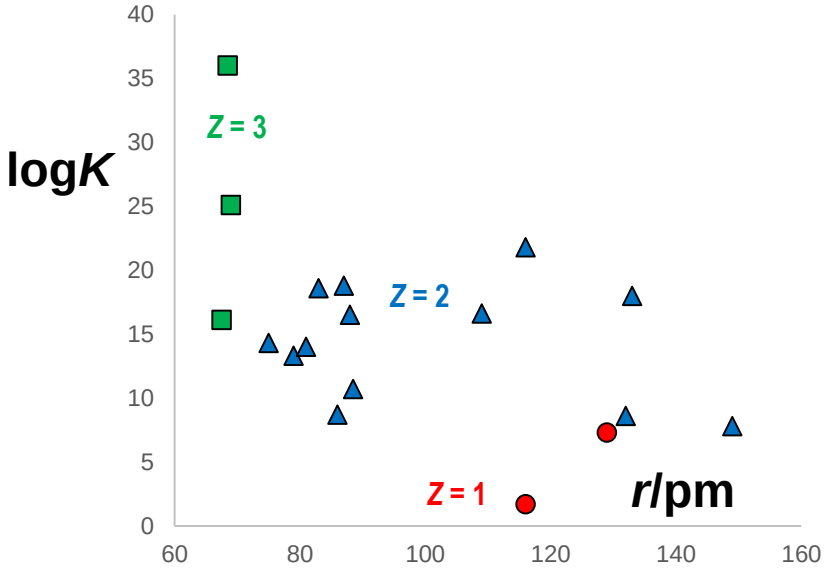
    Mn(II) < Fe(II) < Co(II) < Ni(II) < Cu(II) > Zn(II)
  - Za isti ligand atom s većom energijom ionizacije čini stabilniji kompleks

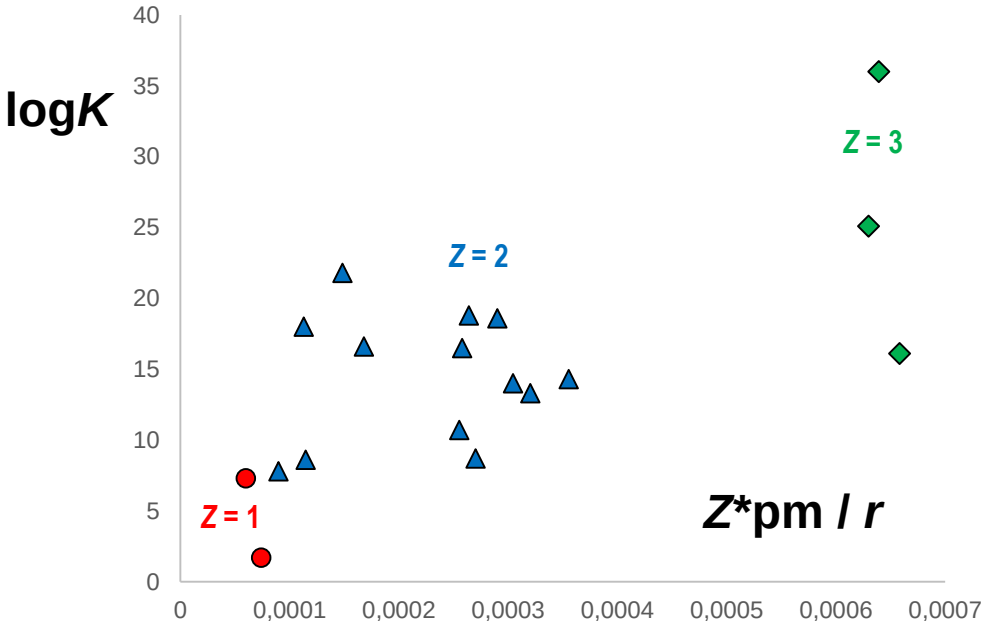
Konstanta stabilnosti

1. Ukupna (kumulativna)

Kompleksi s EDTA







2. Stupnjevita

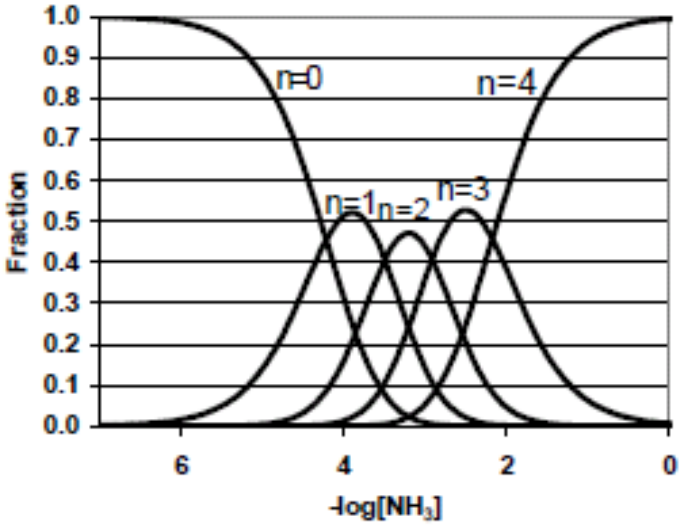
Zamjena liganada jednog za drugim

$[Cu(OH_2)_4]^{2+} + NH_3 \rightleftharpoons [Cu(OH_2)_3(NH_3)]^{2+} + H_2O$ $\quad \log k_1 = 4.22$

$[Cu(OH_2)_3(NH_3)]^{2+} + NH_3 \rightleftharpoons [Cu(OH_2)_2(NH_3)_2]^{2+} + H_2O$ $\quad \log k_2 = 3.50$

$[Cu(OH_2)_2(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(OH_2)(NH_3)_3]^{2+} + H_2O$ $\quad \log k_3 = 2.92$

$[Cu(OH_2)(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + H_2O$ $\quad \log k_4 = 2.18$



Komponente stupnjevitih konstanti

Bjerrum (J.), 1941.

$$T_{n,n+1} = \log \frac{k_n}{k_{n+1}} = S_{n,n+1} + L_{n,n+1}$$

$$L_{n,n+1} = E_{n,n+1} + R_{n,n+1}$$

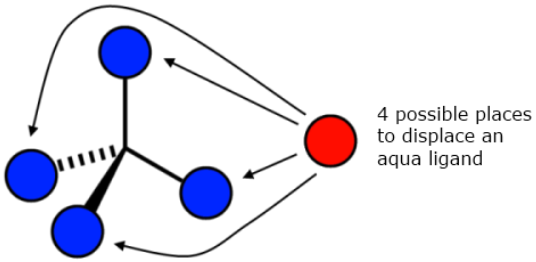
$$\Rightarrow k_n = k_{Sn} k_{En} k_{Rn}$$

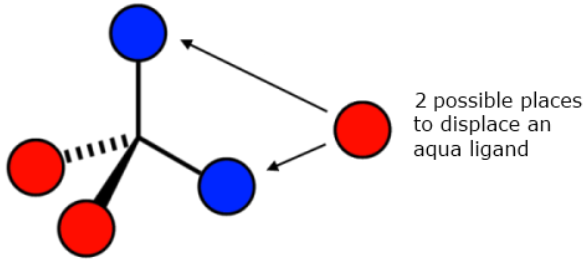
S – Statistički doprinos.

E – Elektristatski doprinos

R – Ostali doprinosi

$S_{n,n+1}$





$$\frac{k_n}{k_{n+1}} = \frac{N-n-1}{N-n}\,\frac{n+1}{n}$$

$$\frac{k_n}{k_{Sn}} = \sqrt[N]{\prod_{j=1}^{N} k_j}$$

N	k_{Sn}^{-1}			
1	1			
2	1/2	2		
3	1/3	1	3	
4	1/4	2/3	3/2	4

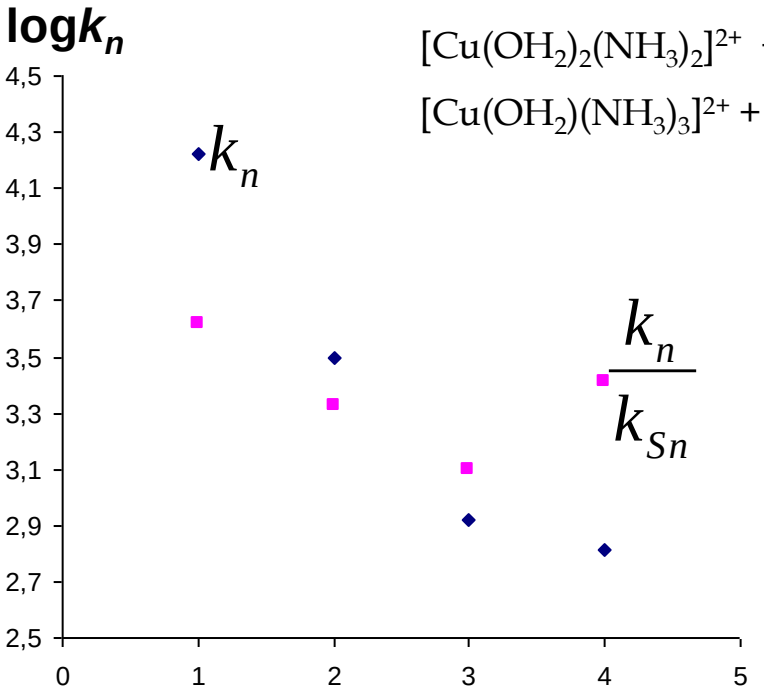
Za $[Cu(NH_3)_n]^{2+}$

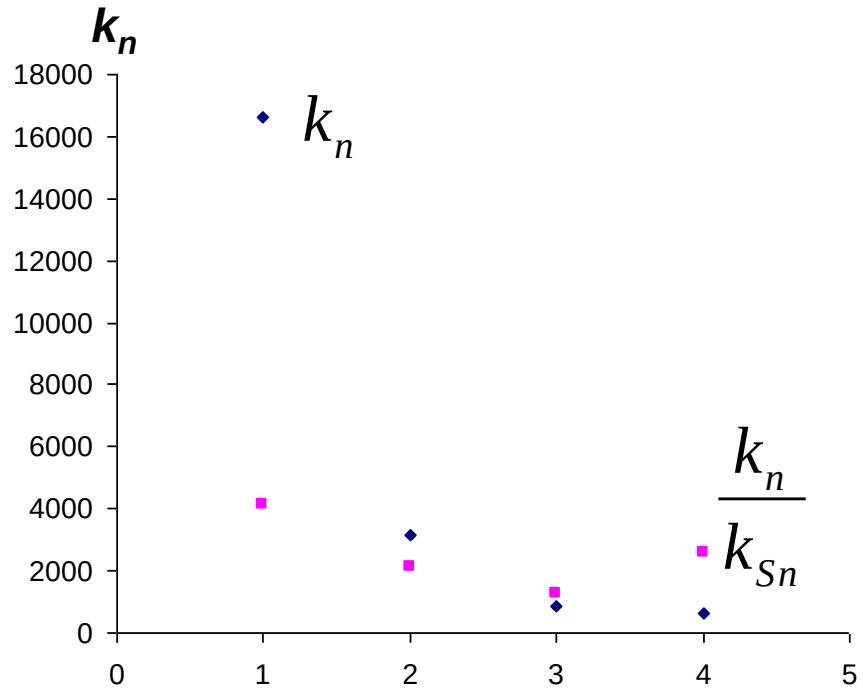
$[Cu(OH_2)_4]^{2+} + NH_3 \rightleftharpoons [Cu(OH_2)_3(NH_3)]^{2+} + H_2O$ $\log k_1 = 4.22$

$[Cu(OH_2)_3(NH_3)]^{2+} + NH_3 \rightleftharpoons [Cu(OH_2)_2(NH_3)_2]^{2+} + H_2O$ $\log k_2 = 3.50$

$[Cu(OH_2)_2(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(OH_2)(NH_3)_3]^{2+} + H_2O$ $\log k_3 = 2.92$

$[Cu(OH_2)(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + H_2O$ $\log k_4 = 2.18$



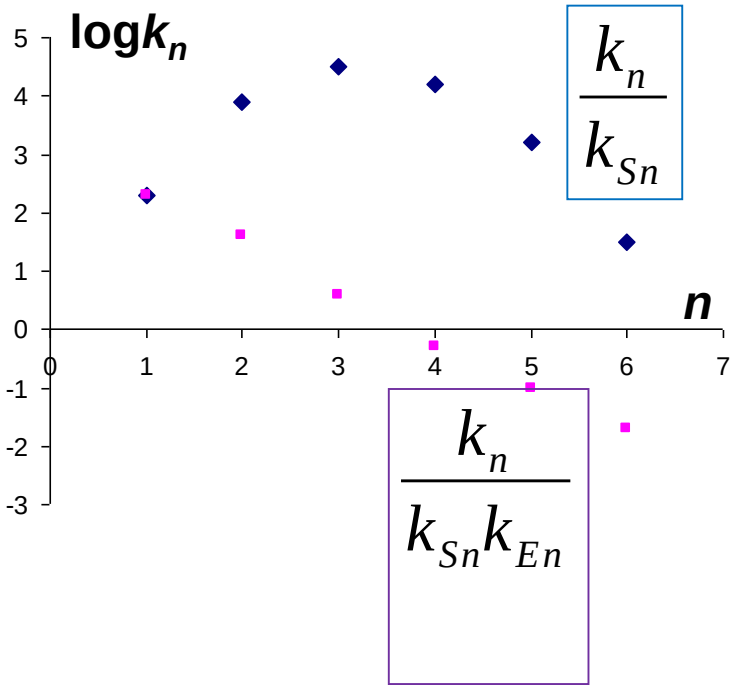


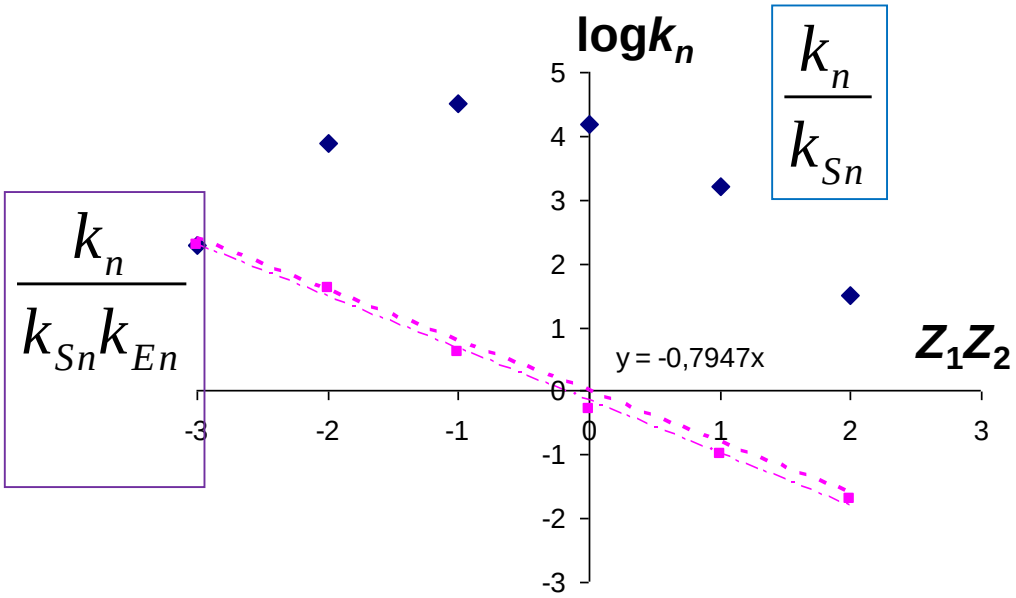
$$E_{n,n+1}$$

$$E_{n,n+1} = f\,\frac{\varphi_{n,n+1}}{kT}$$

$$\varphi_{n,n+1} = \frac{Z_1 Z_2}{\varepsilon r}$$

Za $[Fe(SCN)_n]^{(3-n)+}$





$R_{n,n+1}$

Ukazuje na ‘kemijske’ uzroke razlika stabilnosti pojedinih kompleksa:

- nagla promjena u R – mijenja se koordinacijski poliedar
- periodična promjena u R – *trans* utjecaj
- ...

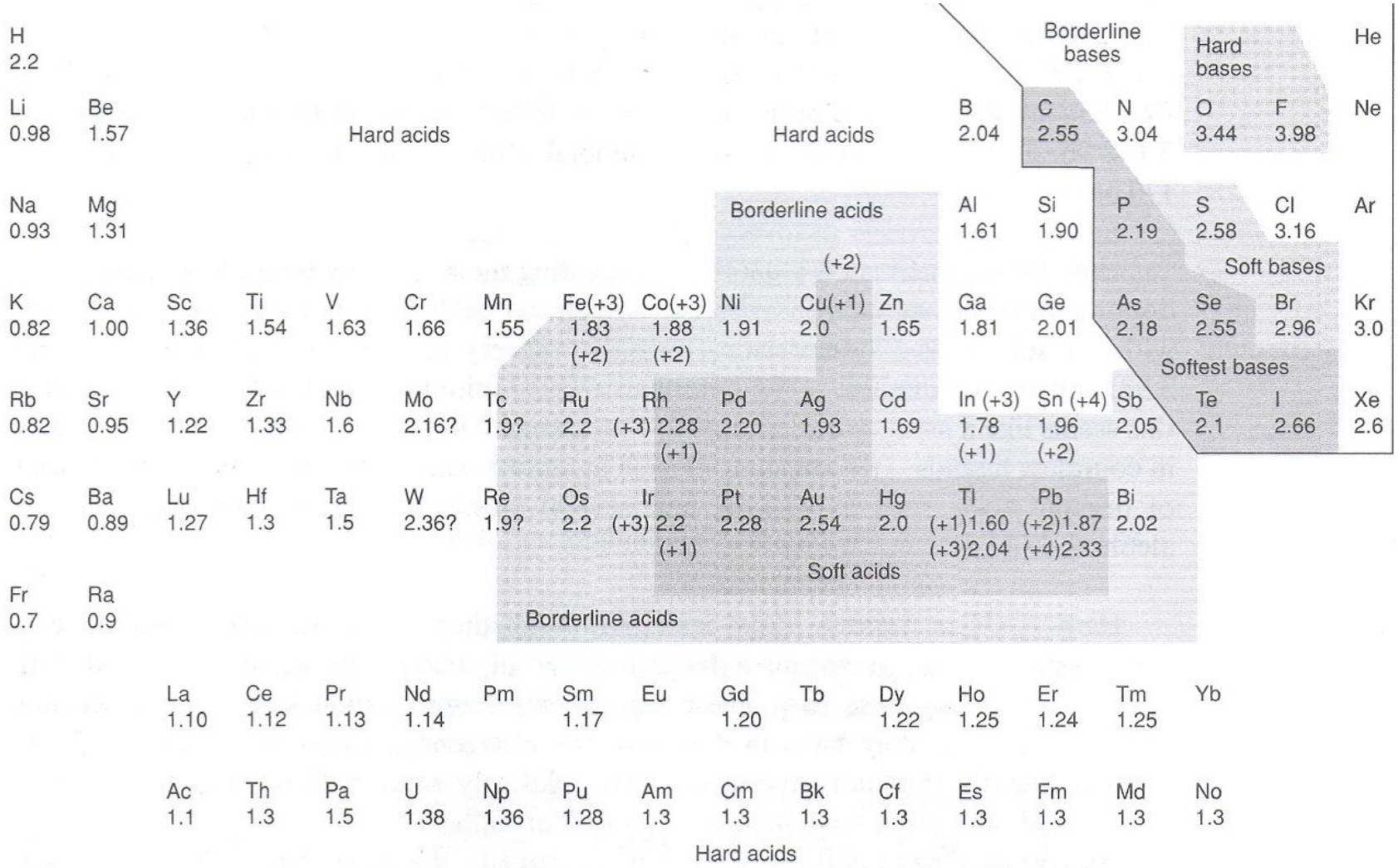
Stabilnost i HSAB

- Reakcija dvostruke izmjene tipa

HA:SB + SA:HB → HA:HB + SA:SB

najčešće je termodinamički povoljna

Tvrde i meke kiseline i baze u PSE

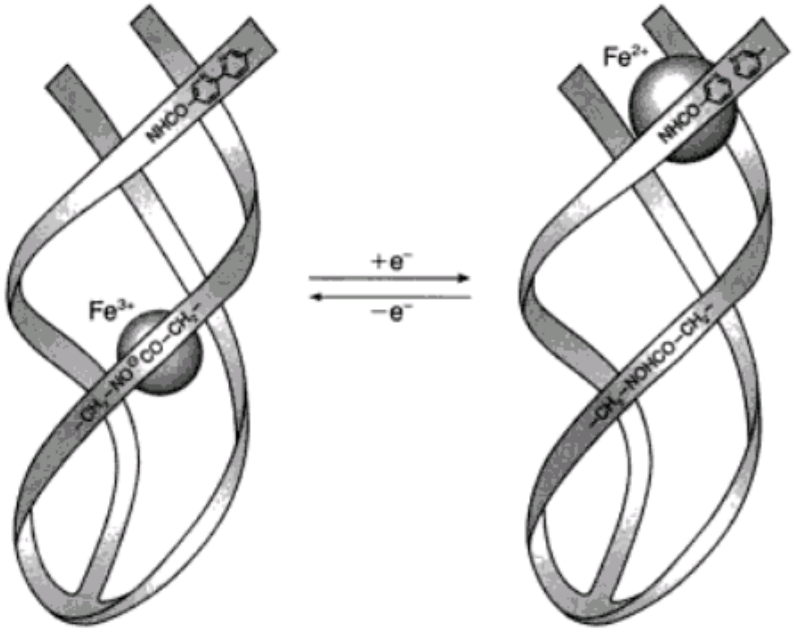


H 2.2																He
Li 0.98	Be 1.57										B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31										Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe(+3) 1.83 (+2)	Co(+3) 1.88 (+2)	Ni 1.91	Cu(+1) 2.0	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.0
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16?	Tc 1.9?	Ru 2.2	Rh (+3) 2.28 (+1)	Pd 2.20	Ag 1.93	Cd 1.69	In (+3) 1.78 (+1)	Sn (+4) 1.96 (+2)	Sb 2.05	Te 2.1	I 2.66	Xe 2.6
Cs 0.79	Ba 0.89	Lu 1.27	Hf 1.3	Ta 1.5	W 2.36?	Re 1.9?	Os 2.2	Ir (+3) 2.2 (+1)	Pt 2.28	Au 2.54	Hg 2.0	Tl (+1) 1.60 (+3) 2.04	Pb (+2) 1.87 (+4) 2.33	Bi 2.02			
Fr 0.7	Ra 0.9																

La 1.10	Ce 1.12	Pr 1.13	Nd 1.14	Pm	Sm 1.17	Eu	Gd 1.20	Tb	Dy 1.22	Ho 1.25	Er 1.24	Tm 1.25	Yb
Ac 1.1	Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.3	Cm 1.3	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3

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

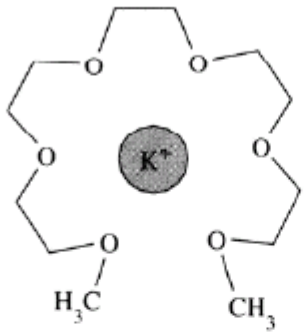
- Tvrdi kationi preferirat će koordinaciju tvrdim bazama (halogeni, O, (N)...)
- Mekani kationi preferirat će koordinaciju mekanim bazama (S, Se, P...)



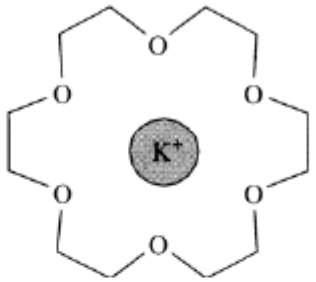
Kelatni i makrociklički učinak

$K[O(CH_3)_2]_6^+$

Very low stability



[K⁺-**3.11**]



[K⁺-**3.6**]

Log *K* (MeOH, 25°C)	2.0	6.1

Complex	ΔG^o (J mol^{-1})	ΔH^o (J mol^{-1})	ΔS^o (J K^{-1} mol^{-1})
[$K^+ \subset$ **3.11**]	−11 368	−36 400	−84
[$K^+ \subset$ **3.6**]	−34 842	−56 000	−71

Kelatni učinak

- Spojevi s kelatirajućim ligandima stabilniji od onih s monodentatnima
  - Entropijska stabilizacija

$$[Ni(NH_3)_6]^{3+} + 3\ NH_2CH_2CH_2NH_2 \rightleftharpoons [Ni(NH_2CH_2CH_2NH_2)_3]^{3+} + 6\ NH_3$$

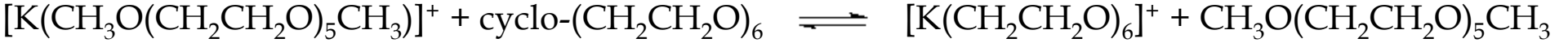
$\Delta_r G$ = -67 kJ/mol

$\Delta_r H$ = -13 kJ/mol

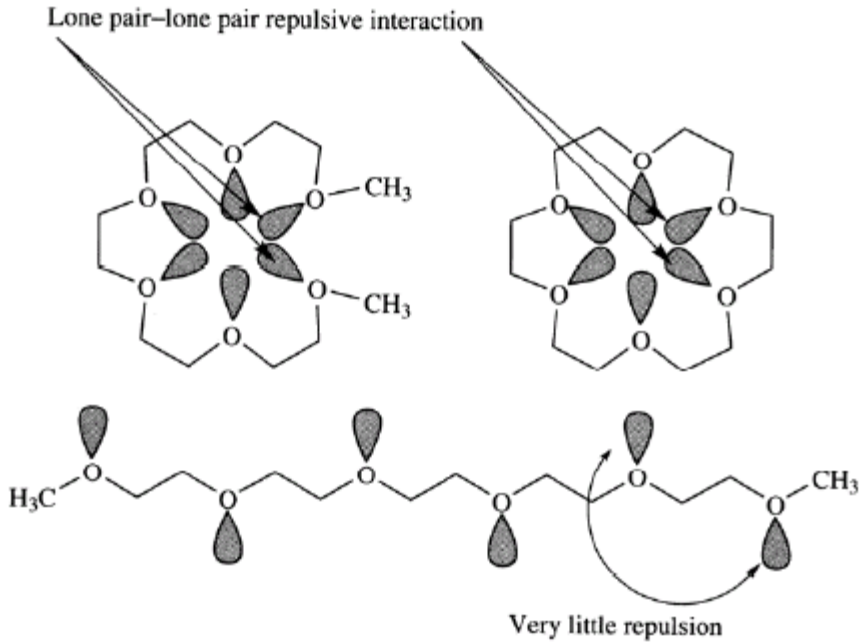
$T\ \Delta_r S$ = 54 kJ/mol

Makrociklički učinak

- Spojevi s makrocikličkim ligandima stabilniji od onih s kelatirajućim
  - Entalpijska i entropijska stabilizacija

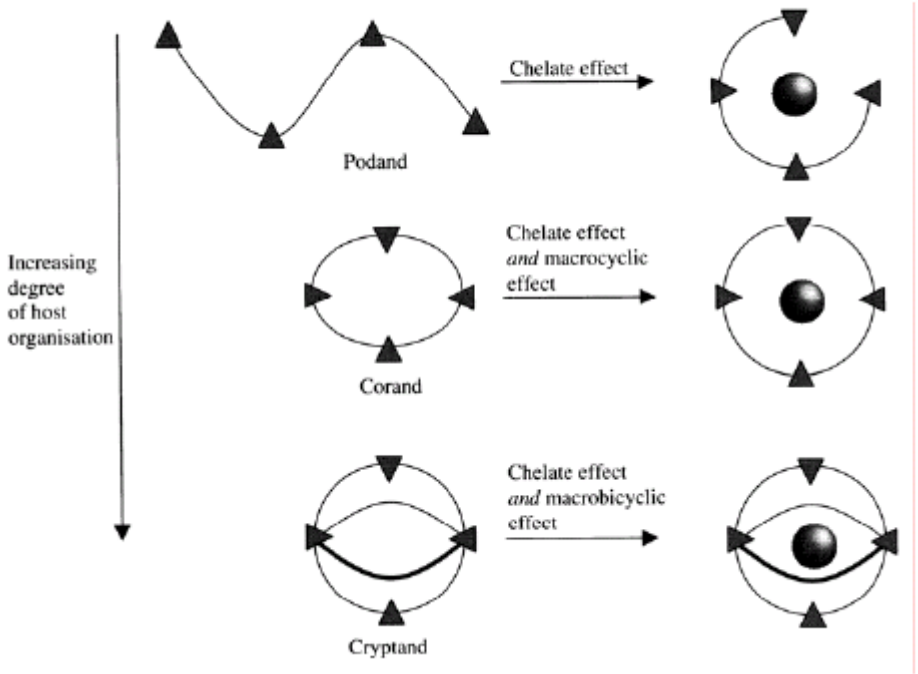


$K \approx 10^4$

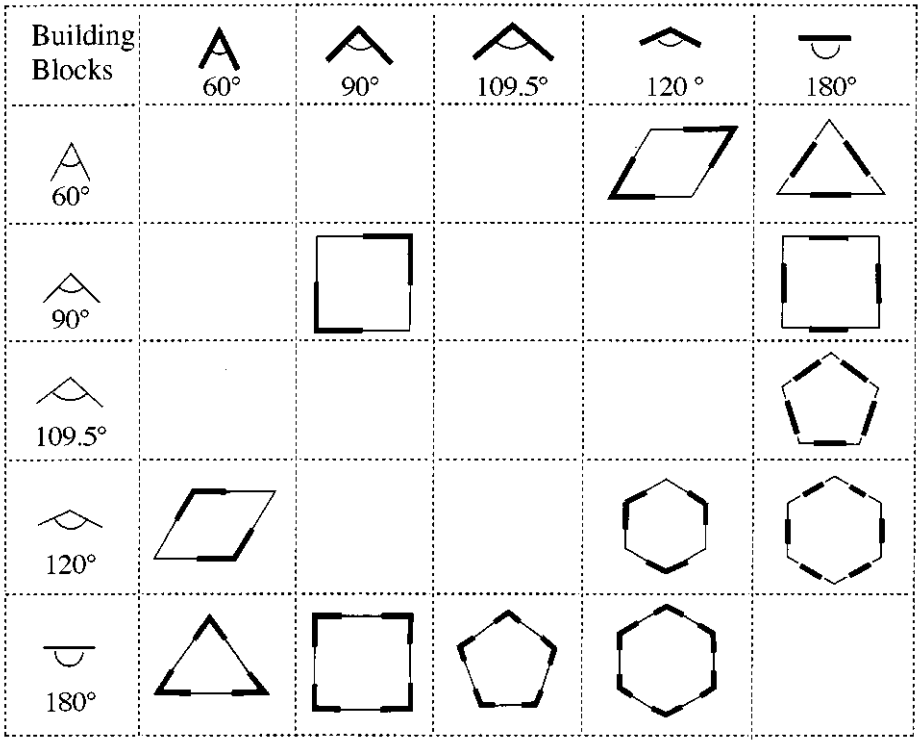


Konformacija kelatirajućeg liganda potrebna za koordinaciju nužno uključuje približavanje veznih mjesta (donirajući elektronski parovi) – entalpijski nepovoljno)

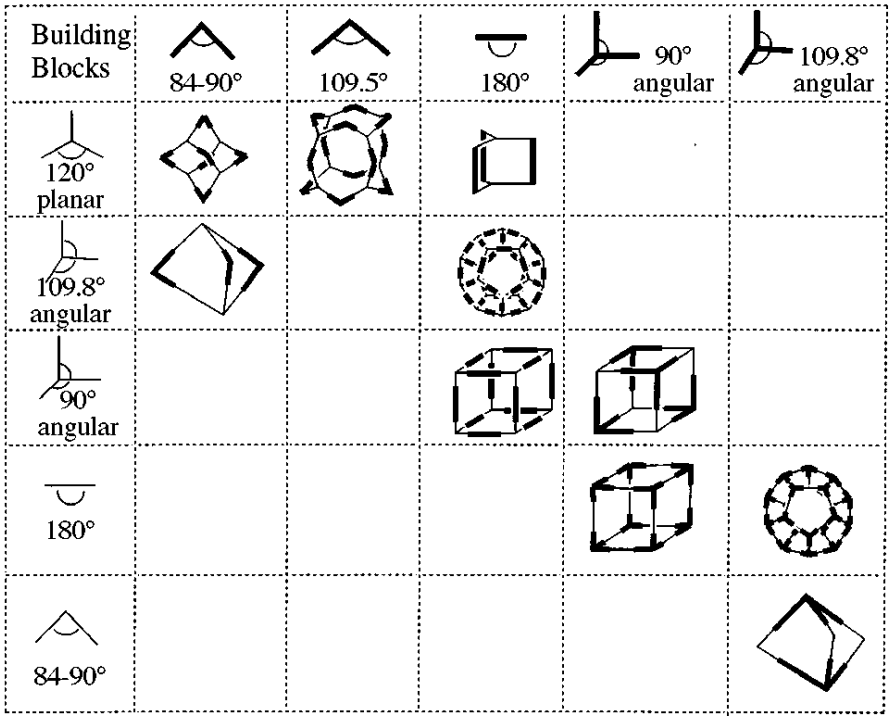
Makrociklički ligand unaprijed ‘ukočen’ u potrebnoj konformaciji – nema entalpijske ‘kazne’ promjene konformacije

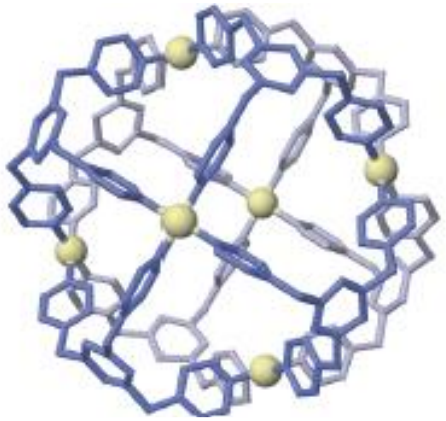


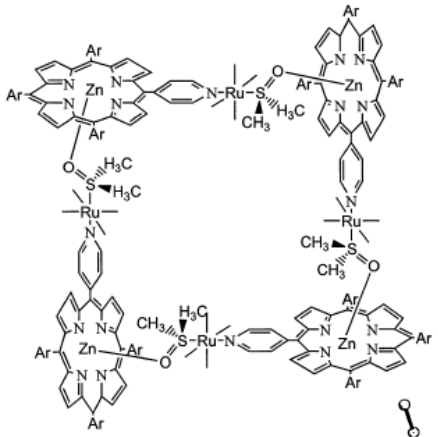
Metalocikli

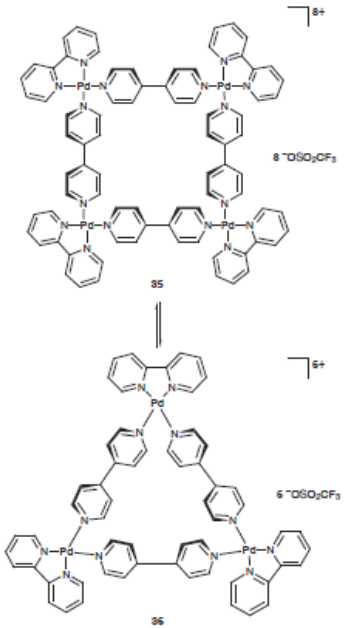


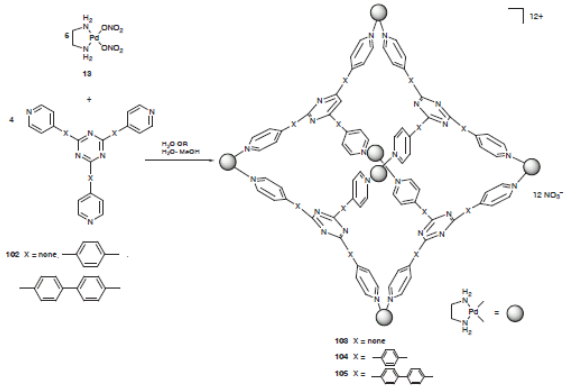
2D i 3D strukture izvedene iz metalnih kationa i premošćujućih liganada

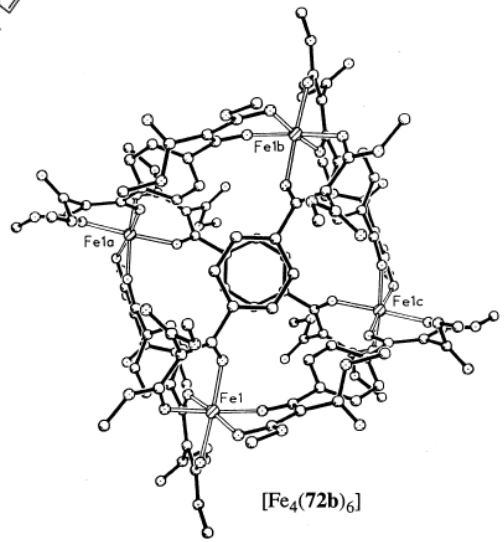




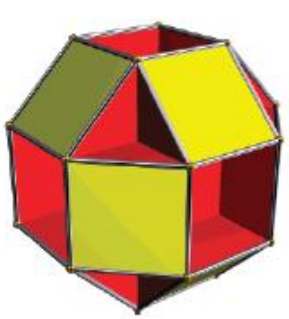


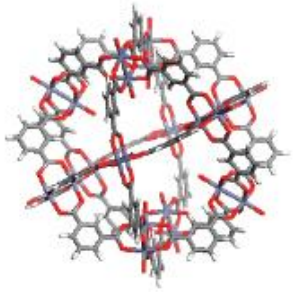






$[Fe_4(\mathbf{72b})_6]$





-pravilni poligoni i poliedri

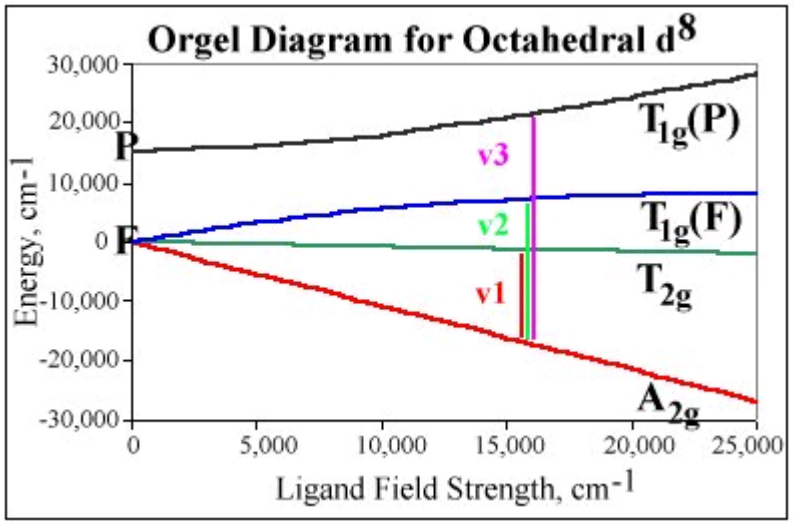
-termodinamički stabilni (u otopini)

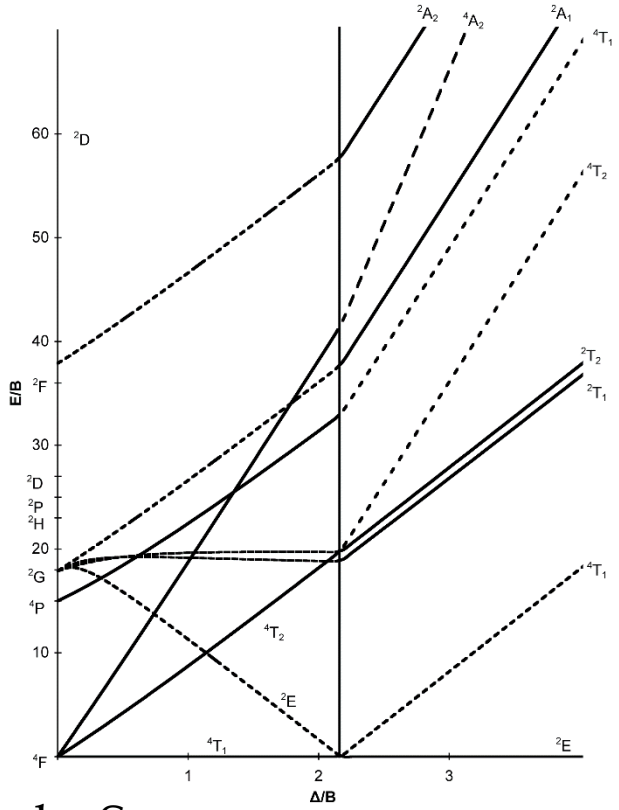
Boja

- Elektronski prijelazi
  - Spektar ligandnog polja („*d*−*d*-prijelazi”)
    - 10000 cm^{-1} – 30000 cm^{-1}
  - Prijenos naboja s liganda na metal
    - Većina vidljivoga spektra
  - Prijenos naboja s metala na ligand
    - UV
  - Unutarligandni prijelazi
    - Najčešće UV, ne ovise jako o koordinaciji

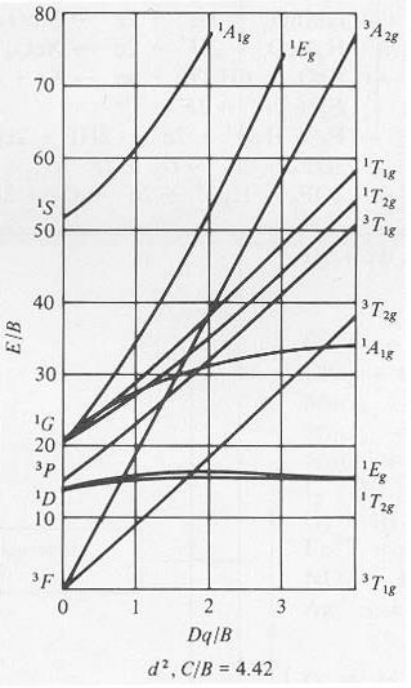
Ligandno polje

- Teorija kristalnog polja
- Teorija ligandnog polja

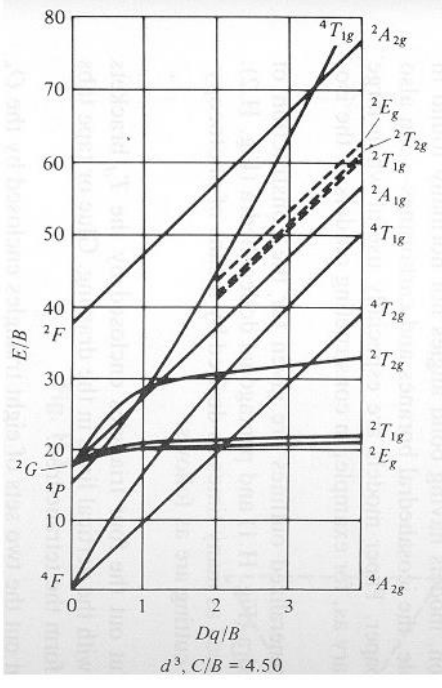




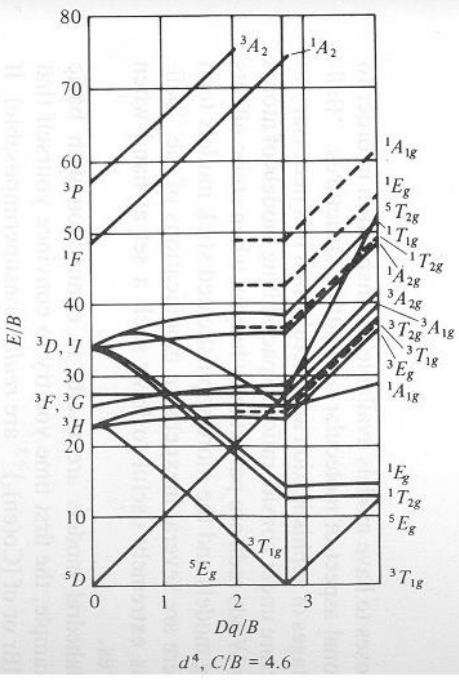
Tanabe-Sugano



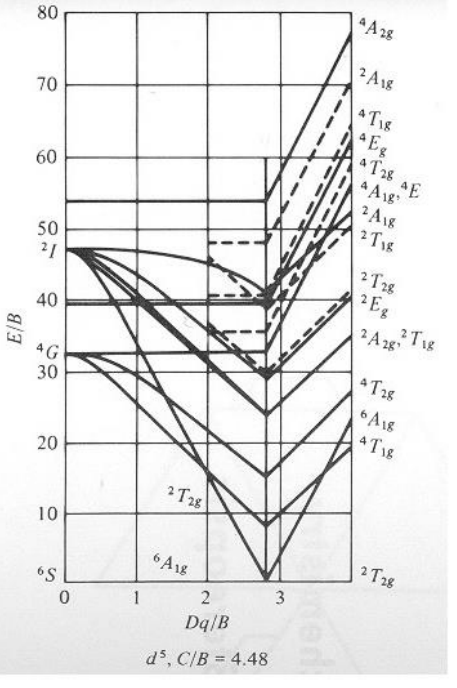
d^2, $C/B = 4.42$



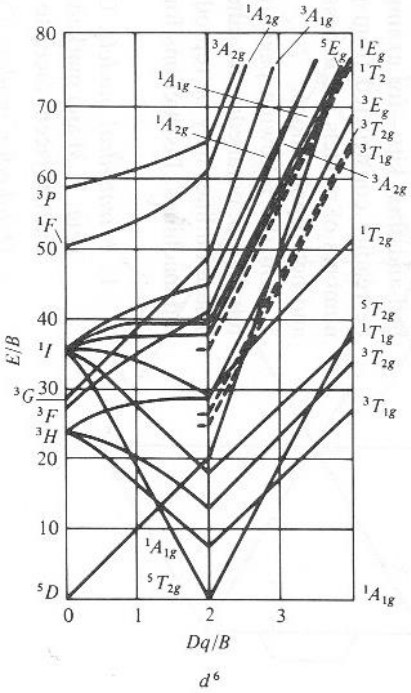
d^3, $C/B = 4.50$



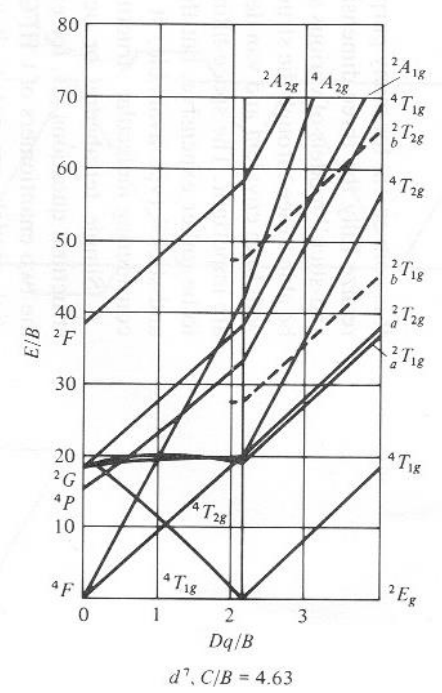
d^4, $C/B = 4.6$



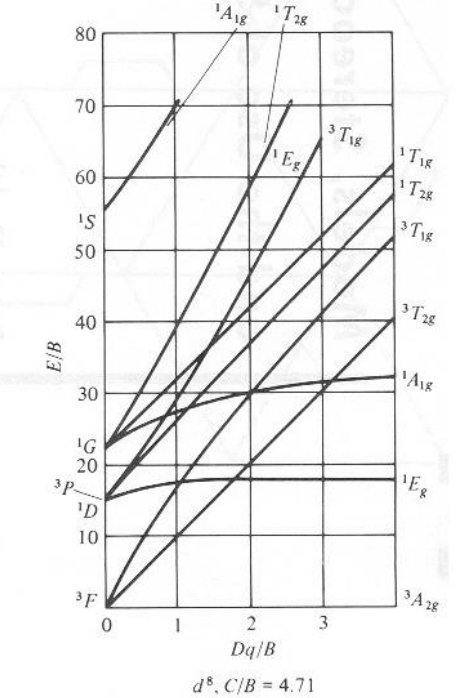
d^5, $C/B = 4.48$



d^6



d^7, $C/B = 4.63$



d^8, $C/B = 4.71$

Magnetska svojstva

- Funkcija broja nesparenih elektrona
- – dijamagnetični i paramagnetični

$$\mu_s = \sqrt{n(n+2)}\ \text{BM}$$

$$1\,\text{BM} = \frac{eh}{4\pi m_e c}$$

- Opadanje magnetskog momenta uslijed (djelomičnog) sparivanja elektrona
  - Domenska struktura – fero i antiferomagnetizam

Određivanje stupnjevitih konstanti

Bodländer, Morse, Bjerrum (N.), Abegg, Jacques,
određivanje srednjeg koordinacijskog broja (do 1914.)

$$\bar{n} = \frac{c(\mathrm{A}) - [\mathrm{A}]}{c(\mathrm{M})} = \frac{[\mathrm{MA}] + 2[\mathrm{MA}_2] + 3[\mathrm{MA}_3] + \ldots}{[\mathrm{M}] + [\mathrm{MA}] + [\mathrm{MA}_2] + \ldots} = \frac{\sum_{n=1}^{N} n k_n [\mathrm{A}]^n}{1 + \sum_{n=1}^{N} k_n [\mathrm{A}]^n} = \sum_{n=1}^{N} (n - \bar{n}) k_n [\mathrm{A}]^n$$