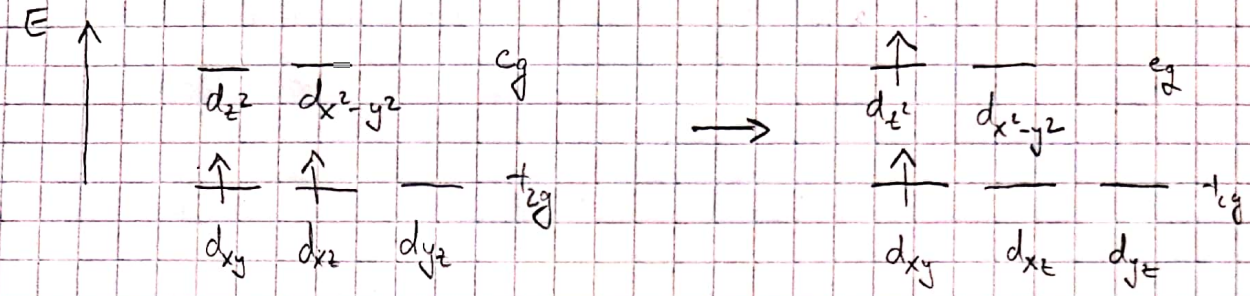
AK2 - Seminar 3

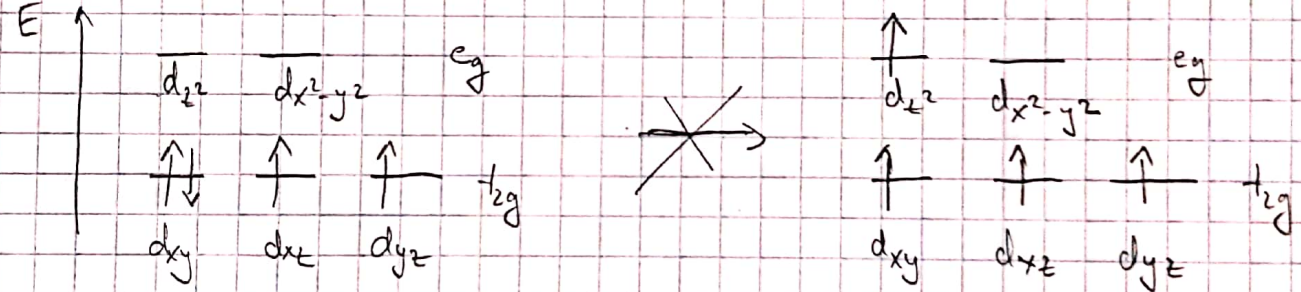
Zadatak 1.

d^2



Prijelaz je SPINSKI DOZVOLJEN jer je ukupna promjena spina 0. ($\Delta S = 0$)

d^4



Prijelaz NIJE SPINSKI DOZVOLJEN jer bi promjena spina bila različita od 0. ($\Delta S \neq 0$)

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Zadatak 2.

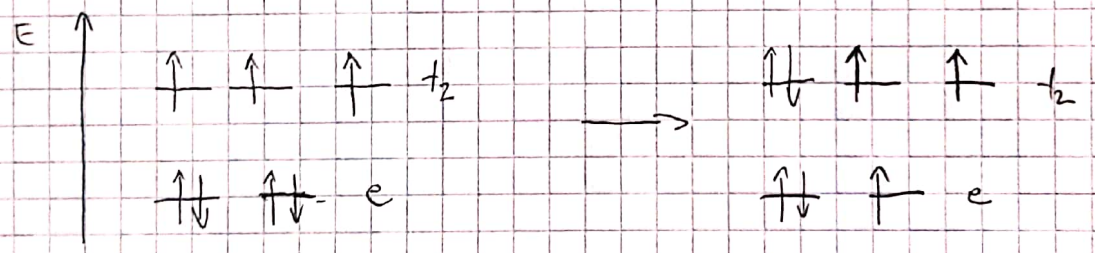
a) $[V(H_2O)_6]^{3+}$ i niskospinski $[Cr(CN)_6]^{4-}$

Elektronski prijelaz je spinski dozvoljen kod niskospinskog $[Cr(CN)_6]^{4-}$. Cr(II) je konfiguracije d^4.
(Vidi zadatak 1)

b) $[CoCl_4]^{2-}$ i $[Co(H_2O)_6]^{2+}$

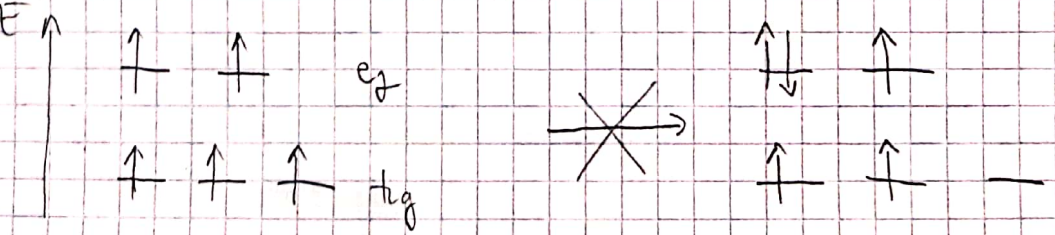
Co(II) je konfiguracije d^7, ε_{max} će biti veća u slučaju tetraedarskog kompleksa zato što su prema LaPorteovom pravilu $d \rightarrow d$ prijelazi zabranjeni u centrosimetričnim okruženjima. Tetraedarski kompleks nema centar simetrije pa će $d \rightarrow d$ prijelaz biti dozvoljen.

Tetraedarsko polje:



c) visokospinski $[Mn(H_2O)_6]^{2+}$ i $[Co(H_2O)_6]^{2+}$

Mn(II)



Prijelaz nije dozvoljen jer ukupna promjena spina mora biti 0 ($\Delta S = 0$)

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Zadatak 3.

$m(\text{uzorak}) = 0{,}2571\ g$

$m(Cu_2S) = 0{,}0641\ g$

$m(KB(ph)_4) = 0{,}2883\ g$

$$n(Cu_2S) = \frac{0{,}0641\ g}{159{,}16\ g\,mol^{-1}} = 4{,}027 \cdot 10^{-4}\ mol$$

$$n(Cu) = 2\,n(Cu_2S) = 8{,}054 \cdot 10^{-4}\ mol$$

$$m(Cu) = 8{,}054 \cdot 10^{-4}\ mol \cdot 63{,}55\ g\,mol^{-1} = 0{,}0512\ g$$

$$\omega(Cu) = \frac{0{,}0512\ g}{0{,}2571\ g} = 19{,}9\ \%$$

$$n_{50mL}(K) = n(KB(ph)_4) = \frac{0{,}2883\ g}{358{,}316\ g\,mol^{-1}} = 8{,}046 \cdot 10^{-4}\ mol$$

$$n_{100mL}(K) = 1{,}609 \cdot 10^{-3}\ mol$$

$$m(K) = 1{,}609 \cdot 10^{-3}\ mol \cdot 39{,}09\ g\,mol^{-1} = 0{,}0629\ g$$

$$\omega(K) = \frac{0{,}0629\ g}{0{,}2571\ g} = 24{,}5\ \%$$

$m(\text{uzorak}) = 0{,}1643\ g$

$m(AgCl) = 0{,}2955\ g$

$$n(Cl) = n(AgCl) = \frac{0{,}2955\ g}{143{,}32\ g\,mol^{-1}} = 2{,}062 \cdot 10^{-3}\ mol$$

$$m(Cl) = 2{,}062 \cdot 10^{-3}\ mol \cdot 35{,}45\ g\,mol = 0{,}0731\ g$$

$$\omega(Cl) = \frac{0{,}731\ g}{0{,}1643\ g} = 44{,}5\ \%$$

$\omega(H_2O) = 11{,}1\ \%$

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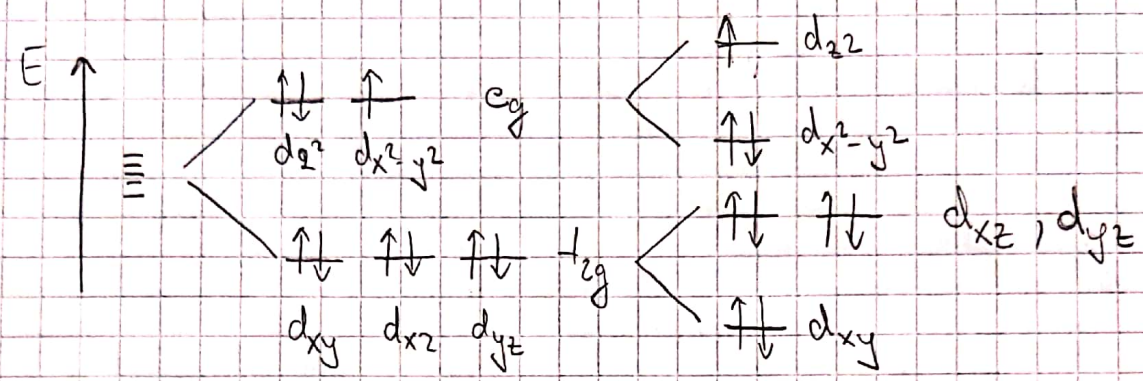
$\frac{19,9\ g}{63,55\ g\,mol^{-1}} : \frac{24,5\ g}{39,09\ g\,mol^{-1}} : \frac{44,5\ g}{35,45\ g\,mol^{-1}} : \frac{11,1\ g}{18,01\ g\,mol^{-1}}$

$0,3131\ mol : 0,6267\ mol : 1,2553\ mol : 0,6163\ mol \;/: 0,3131\ mol$

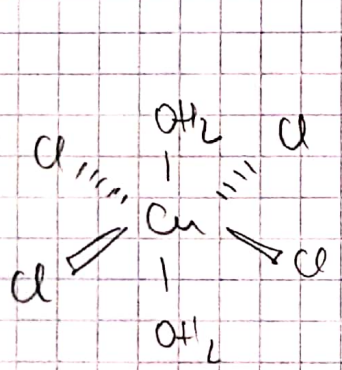
$1 : 2 : 4 : 2$

$K_2[CuCl_4(H_2O)_2]$ kalijev diakvatetrakloridokuprat(II)



Jahn-Tellerov efekt - ako je osnovno elektronsko stanje nelinearnog kompleksa orbitalno degenerirano i asimetrično popunjeno, tada se kompleks deformira kako bi uklonio degeneraciju i postigao nižu energiju

U ovom slučaju kompleks ima geometriju spljoštenog oktaedra. Cu–H_2O veze su kraće od Cu–Cl.



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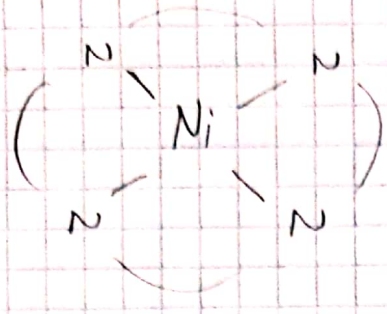
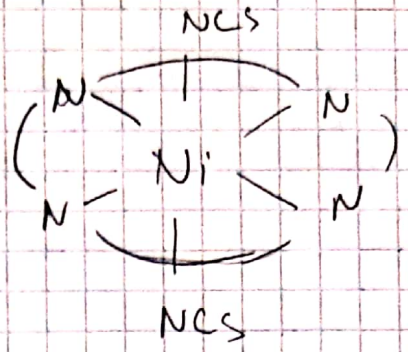
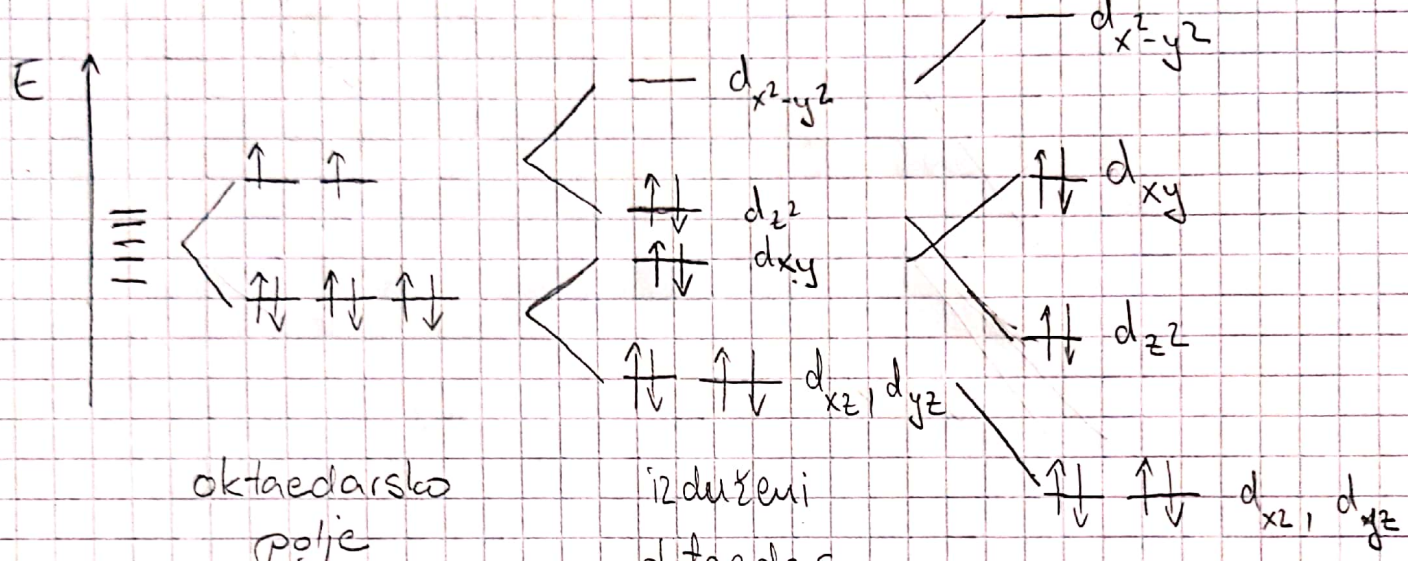
Zadatak 4.



kvadratni kompleks



oktaedarski kompleks



oktaedarsko polje → paramagnetično

izduženi oktaedar

kvadratno polje → dijamagnetično

Ako zamislimo da oktaedarskom kompleksu ligande koji su u smjeru z-osi udaljavamo od metalnog centra, sve orbitale koje sadrže z komponentu će biti niže energije. Ako se ligandi dovoljno udalje, nastaje kvadratni kompleks pri čemu dolazi do sparivanja elektrona zbog čega je u slučaju Ni(II) kvadratni kompleks dijamagnetičan.

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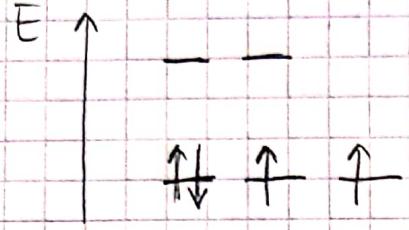
Zadatak 5.

a) KELAT (grč. kandža) - kompleks u kojem ligand formira prsten koji uključuje metalni atom.

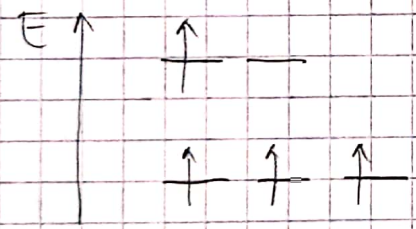
b) $[Mn(NH_3)_6]^{3+}$



$$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} = 2{,}83$$

n – broj nesparenih elektrona

$[MnF_6]^{3-}$



$$\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = 4{,}89$$

c) vidi zadatak 4

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Zadatak 6.

KOMPLEKS B:

$m(\text{uzorak}) = 0{,}1285\ g$

$m(Ni(C_4H_7O_2N_2)_2) = 0{,}1445\ g$

$n(Ni) = n(Ni(dmg)_2) = \frac{0{,}1445\ g}{288{,}9226\ g\,mol^{-1}} = 5 \cdot 10^{-4}\ mol$

$w(Ni) = \frac{5 \cdot 10^{-4}\ mol \cdot 58{,}7\ g\,mol^{-1}}{0{,}1285\ g} = 22{,}8\ \%$

$m(\text{uzorak}) = 5{,}138\ mg$

$m(CO_2) = 8{,}801\ mg$

$m(H_2O) = 2{,}539\ mg$

$n(C) = n(CO_2) = \frac{8{,}801\ mg}{44{,}009\ g\,mol} = 1{,}9 \cdot 10^{-4}\ mol$

$w(C) = \frac{1{,}9 \cdot 10^{-4}\ mol \cdot 12{,}011\ g\,mol^{-1}}{5{,}138 \cdot 10^{-3}\ g} = 46{,}7\ \%$

$n(H) = 2n(H_2O) = 2 \cdot \frac{2{,}539\ mg}{18{,}0148\ g\,mol^{-1}} = 2{,}8 \cdot 10^{-4}\ mol$

$w(C) = \frac{2{,}8 \cdot 10^{-4}\ mol \cdot 1{,}0079\ g\,mol}{5{,}138 \cdot 10^{-3}\ g} = 5{,}5\ \%$

$w(O) = 25{,}0\ \%$

$\frac{22{,}8\ g}{58{,}7\ g\,mol^{-1}} : \frac{46{,}7\ g}{12{,}011\ g\,mol^{-1}} : \frac{5{,}5\ g}{1{,}0079\ g\,mol^{-1}} : \frac{25\ g}{15{,}999\ g\,mol^{-1}}$

$0{,}3884\ mol : 3{,}888\ mol : 5{,}4568\ mol : 1{,}5626\ mol \;/: 0{,}3884\ mol$

$1 : 10 : 14 : 4$

$[Ni(C_5H_7O_2)_2]$

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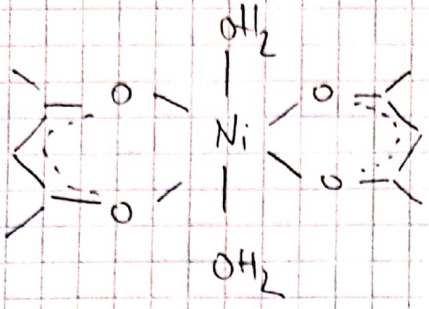
KOMPLEKS A: $[Ni(C_5H_7O_2)_2(H_2O)_2]$



KOMPLEKS C:

$m(\text{uzorak}) = 0{,}236\ g$

$m(Ni) = 0{,}0335\ g$

$$w(Ni) = \frac{0{,}0335\ g}{0{,}236\ g} = 14{,}2\ \%$$

$m(\text{uzorak}) = 0{,}210\ g$

$V(N_2) = 12{,}10\ mL$

$p = 1{,}01325 \cdot 10^5\ Pa$

$T = 293{,}15\ K$

$$w(N) = 2w(N_2) = \frac{pV}{RT} = 2 \cdot \frac{1{,}01325 \cdot 10^5\ Pa \cdot 12{,}10 \cdot 10^{-6}\ m^3}{8{,}314\ J K^{-1} mol^{-1} \cdot 293{,}15\ K}$$

$$= 2 \cdot 5 \cdot 10^{-4}\ mol = 1 \cdot 10^{-3}\ mol$$

$$w(N) = \frac{1 \cdot 10^{-3}\ mol \cdot 14{,}007\ g mol^{-1}}{0{,}210\ g} = 6{,}7\ \%$$

$m(\text{uzorak}) = 8{,}630\ mg$

$m(CO_2) = 18{,}300\ mg$

$m(H_2O) = 4{,}500\ mg$

$$w(C) = w(CO_2) = \frac{18{,}300\ mg}{44{,}009\ g mol^{-1}} = 4{,}1 \cdot 10^{-4}\ mol$$

$$w(C) = \frac{4{,}1 \cdot 10^{-4}\ mol \cdot 12{,}011\ g mol^{-1}}{8{,}630 \cdot 10^{-3}\ g} = 57{,}8\ \%$$

$$w(H) = 2w(H_2O) = 2 \cdot \frac{4{,}500\ mg}{18{,}0148\ g mol^{-1}} = 5 \cdot 10^{-4}\ mol$$

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$$\omega(H) = \frac{5 \cdot 10^{-4}\ mol \cdot 1{,}0079\ g\,mol^{-1}}{8{,}630 \cdot 10^{-3}\ g} = 5{,}8\,\%$$

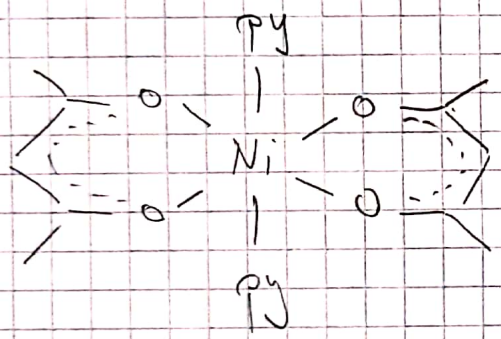
$$\omega(O) = 15{,}5\,\%$$

$$\frac{14{,}2\ g}{58{,}7\ g\,mol^{-1}} : \frac{6{,}7\ g}{14{,}007\ g\,mol^{-1}} : \frac{57{,}8\ g}{12{,}011\ g\,mol^{-1}} : \frac{5{,}8\ g}{1{,}0079\ g\,mol^{-1}} : \frac{15{,}5\ g}{15{,}999\ g\,mol^{-1}}$$

$$0{,}2419\ mol : 0{,}4783\ mol : 4{,}8122\ mol : 5{,}7545\ mol : 0{,}9688\ mol \;/\; : 0{,}2419\ mol$$

1 : 2 : 20 : 24 : 4

$[Ni(C_5H_7O_2)_2(py)_2]$



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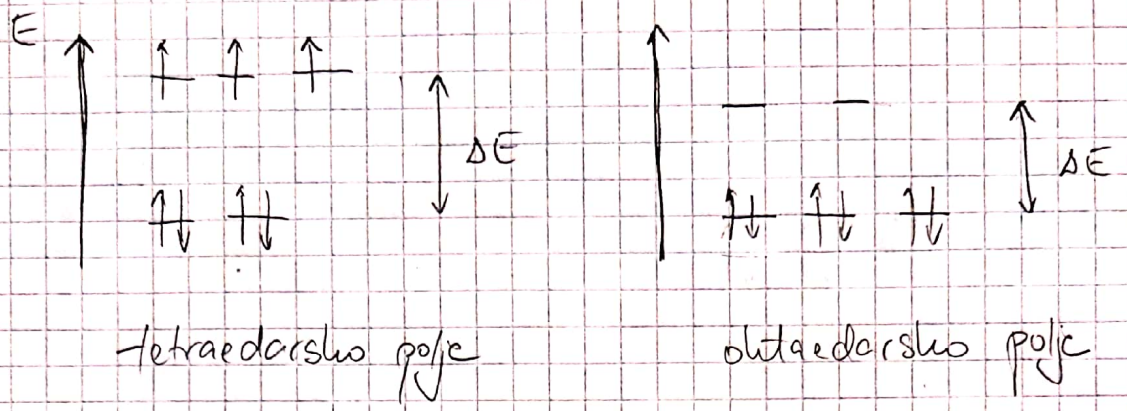
Zadatak 7.

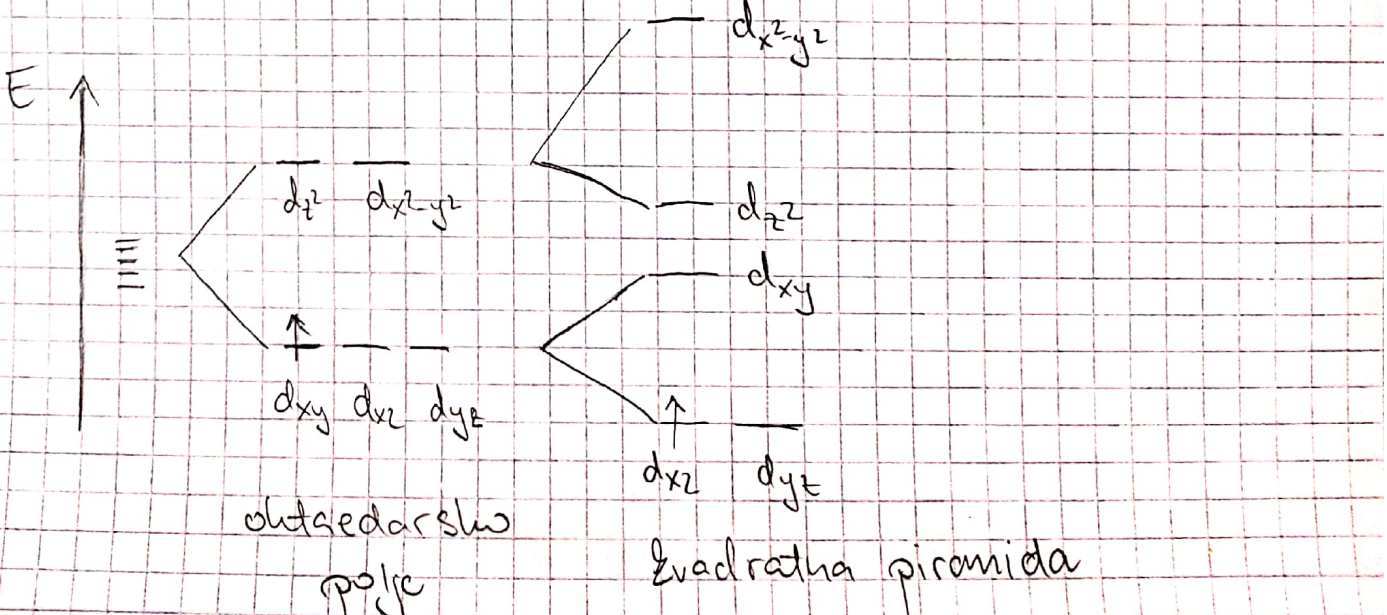
$[Co(NCS)_4]$; $[Co(H_2O)_6]^{2+}$



tetraedarsko polje oktaedarsko polje

SCN^- je ligand koji jako cijepa ligandno polje, dok je H_2O ligand koji slabije cijepa ligandno polje. ΔE je veći za SCN^- ligand. Kada se elektron pobudi u više stanje, prilikom vraćanja u niže stanje emitira svjetlost energije jednake $\frac{hc}{\lambda}$. Za slučaj SCN^-, λ će biti manji pa će svjetlost biti tamnoplava, a za H_2O će λ biti veća, tj. svjetlost će biti roza.

$[VO(acac)_2]$



oktaedarsko polje

kvadratna piramida

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