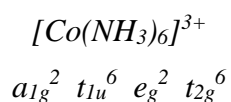


**MOLECULAR ORBITAL THEORY OF COORDINATION COMPOUNDS**

**OCTAHEDRAL COMPLEXES**

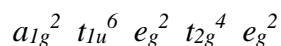
*σ-Bonding*

*In the valence shell of transition metals, there are 9 atomic orbitals (5 d + 1 s + 3 p). For octahedral ML<sub>6</sub> complex, the point group is O<sub>h</sub>. The symmetry of the nine valence orbitals is found from the O<sub>h</sub> point group character table as a<sub>1g</sub> (1s), t<sub>1u</sub> (p<sub>x</sub>, p<sub>y</sub>, p<sub>z</sub>), t<sub>2g</sub> (d<sub>xy</sub>, d<sub>xz</sub>, d<sub>yz</sub>) and e<sub>g</sub> (d<sub>x<sup>2</sup>-y<sup>2</sup></sub>, d<sub>z<sup>2</sup></sub>). In the octahedral complexes, each of the six ligands has an orbital, which is σ-symmetrical around the M-L bond axis and directed to the central atom. Only the ligands forming the σ-bond interact with the hybrid orbitals. Examples of such ligands are H<sub>2</sub>O, NH<sub>3</sub>. This orbital is filled sp<sup>3</sup> hybrid orbital for the NH<sub>3</sub> ligand, and is one of the full 3p orbitals for Cl. In metal, there are atomic orbitals with a<sub>1g</sub>, t<sub>1u</sub>, t<sub>2g</sub> and e<sub>g</sub> symmetry, while the ligand group orbitals are with σ symmetry directed to the metal atom. Orbitals with the same symmetry representation overlap and then the BMOs and AMOs are formed. The ligand group orbitals which do not make any overlapping remain the NMOs.*



$$\Delta_o > p$$

Diamagnetic

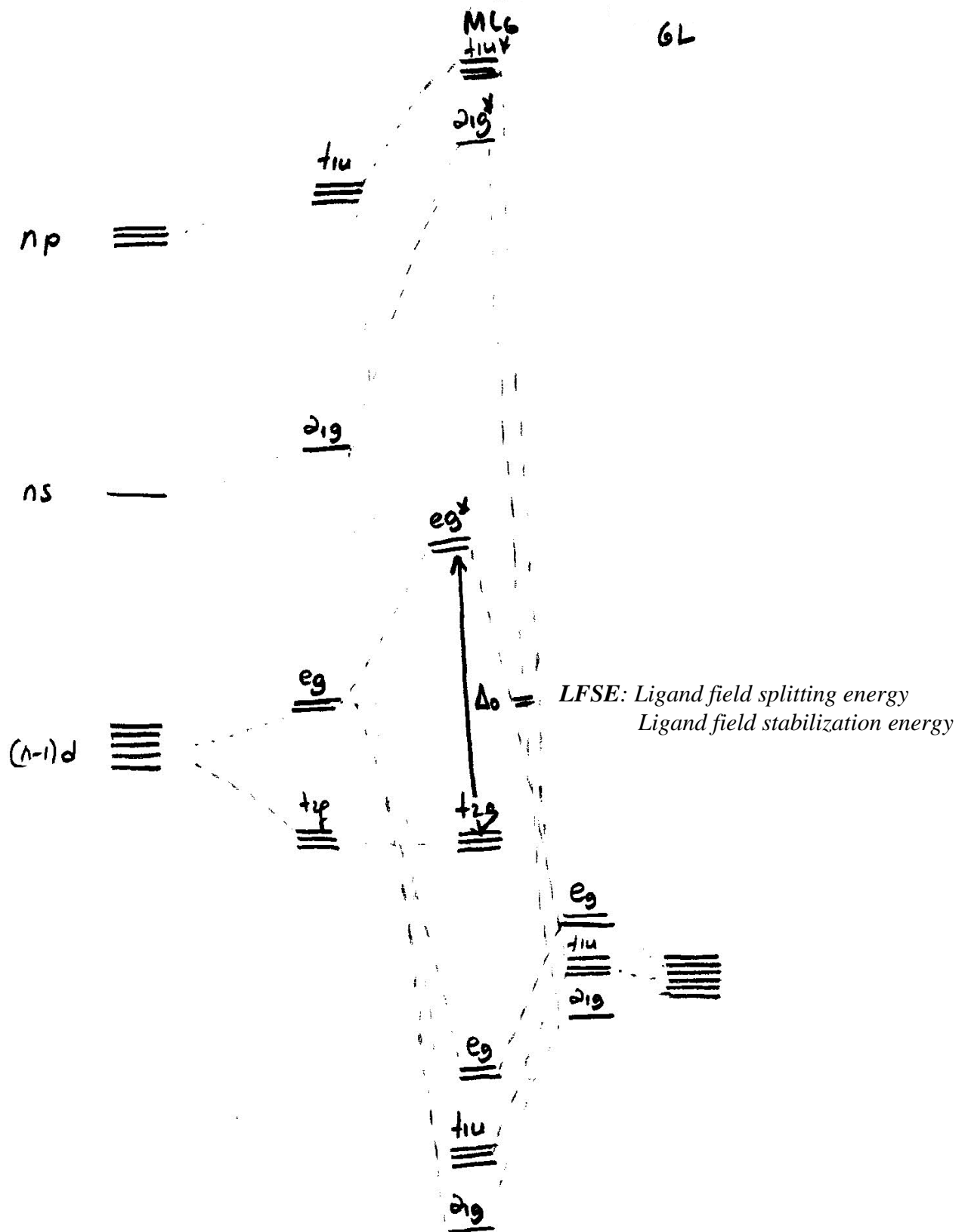


$$\Delta_o < p$$

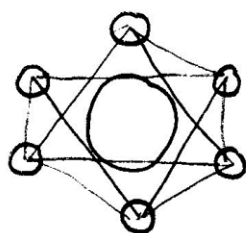
Paramagnetic (4 unpaired electrons)

*t<sub>2g</sub> → e<sub>g</sub> transitions determine the color of complexes. The colors of these complexes are different as the LFSEs are different.*

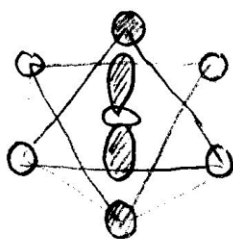
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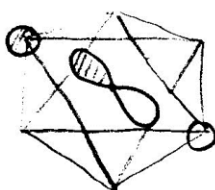
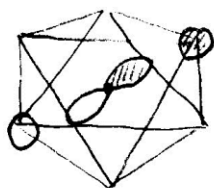
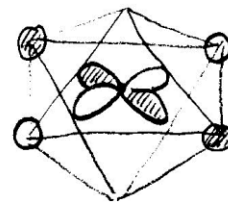
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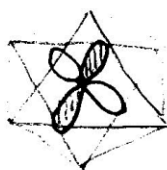
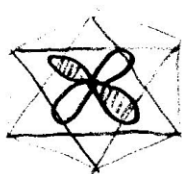
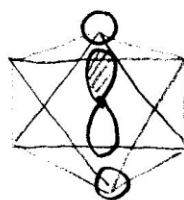
$a_{1g}$



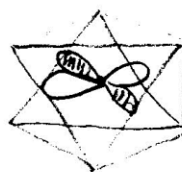
$e_g$



$t_{1u}$



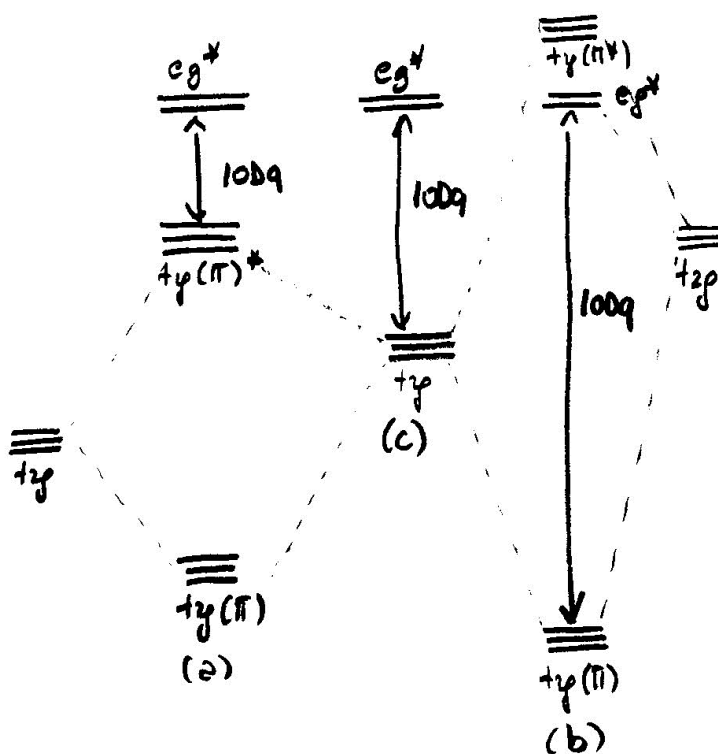
$t_{2g}$



*Ligand group orbitals corresponding to the symmetry of the central atom orbitals which may form the  $\sigma$  bond in octahedral complexes*

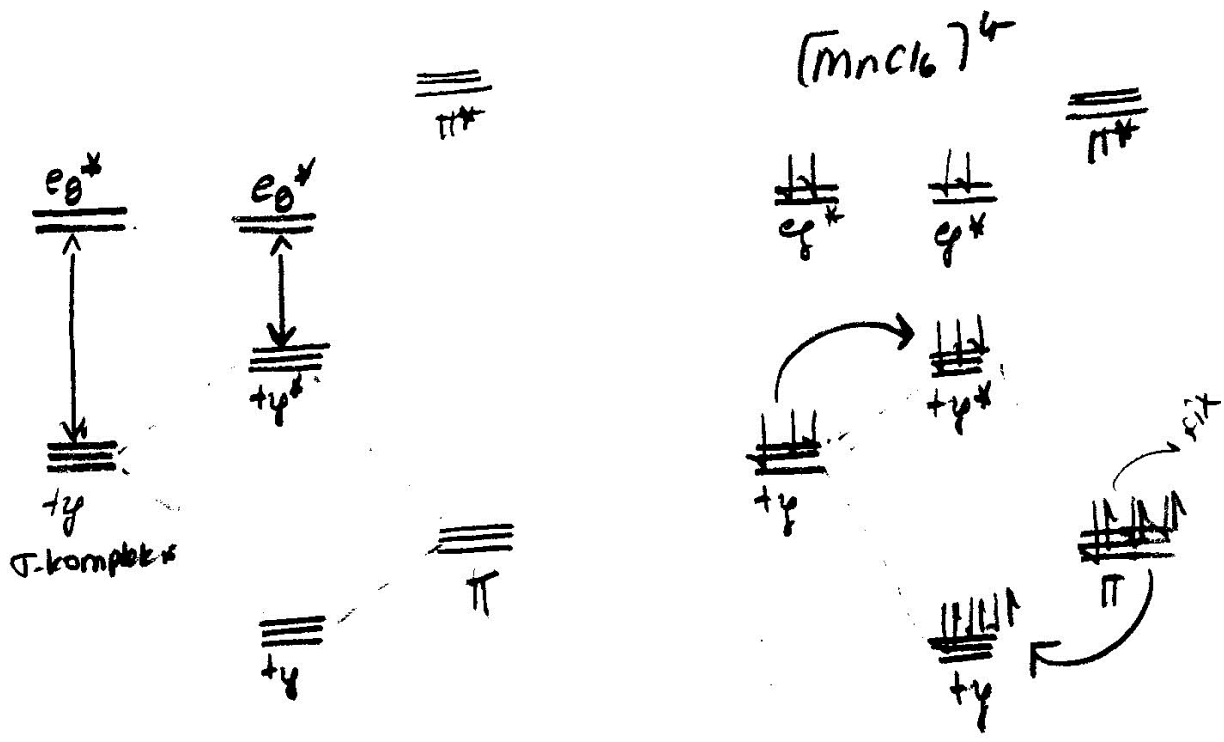
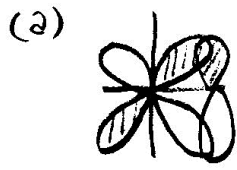
**$\pi$ -Bonding**

The acceptance and explanation of  $\pi$ -bonding indicates that the MOT has a significant advantage over VBT and CAT. The presence of stable metal complexes with low oxidation steps such as  $[\text{Ni}(\text{CO})_4]$  by  $\pi$ -bonding and the order of the ligands forming the spectrochemical series can be explained more satisfactorily. If there are  $\pi$ -symmetric orbitals in the ligands relative to the M-L bond axis, these orbitals can overlap with the  $\pi$ -symmetric orbitals of the metal to form  $\pi$ -symmetric molecular orbitals. The ligands which are capable of  $\pi$ -bonding are divided into Lewis-electron donor (Lewis  $\pi$ -base) ligands and  $\pi$ -electron acceptor (Lewis  $\pi$ -acid) ligands.

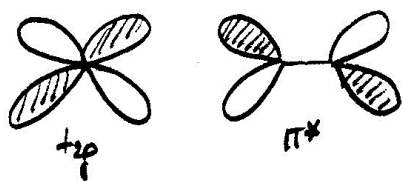


*For  $ML_6$  complexes*  
 (a)  $\pi$ -donor ligand  
 (b)  $\pi$ -acceptor ligand  
 (c)  $\sigma$ -binding ligand

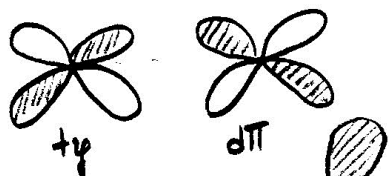
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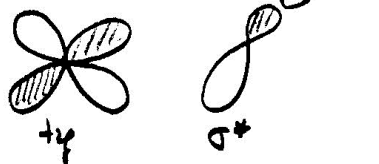
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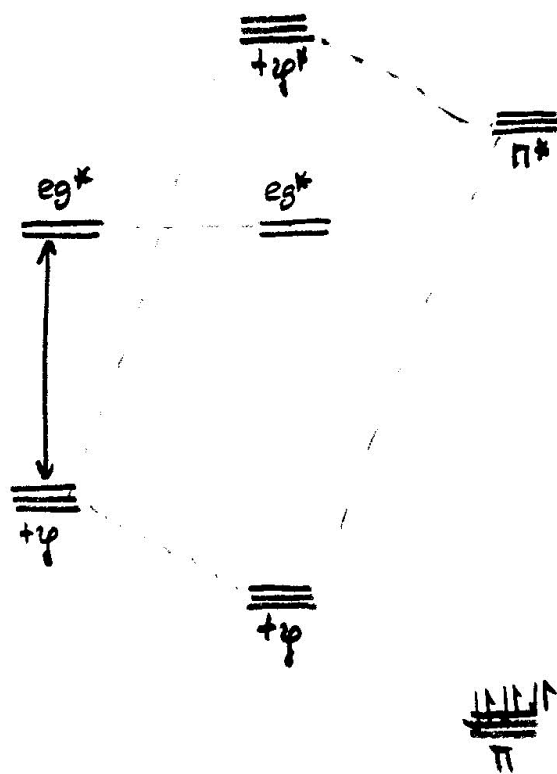
*In the formation of M-CO bond*



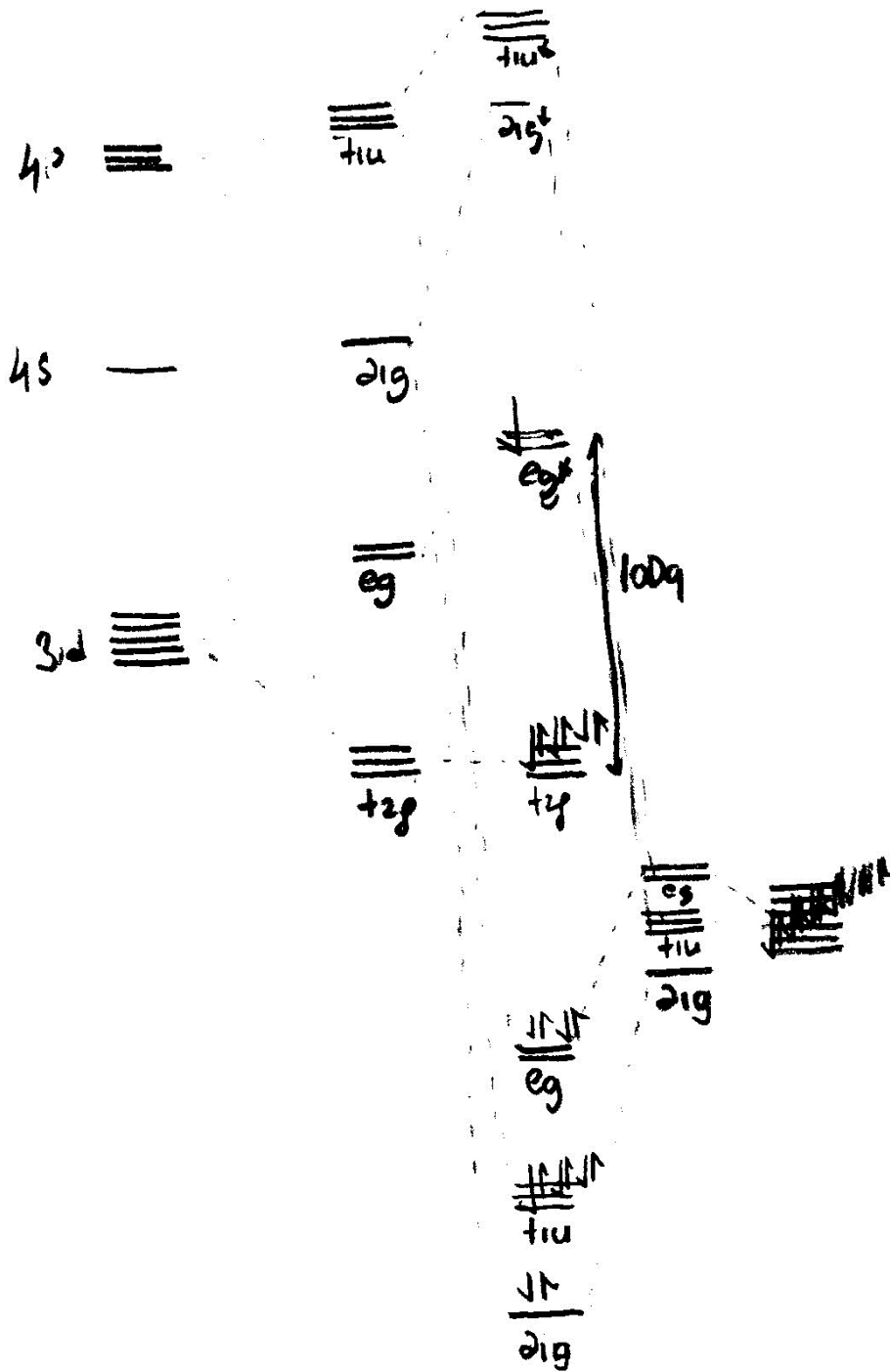
*In the formation of M-PF<sub>3</sub> bond*



*In the formation of M-PF<sub>3</sub> and M-CF<sub>3</sub> bonds*



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$$(2ig)^2 (+1u)^6 (eg)^4 (+4)^6 (eg^*)^1$$

$$BD = \left[ \frac{12-1}{2} \right] / 6 = \frac{11}{12} \quad (\text{for Co-N bond})$$

*paramagnetic*

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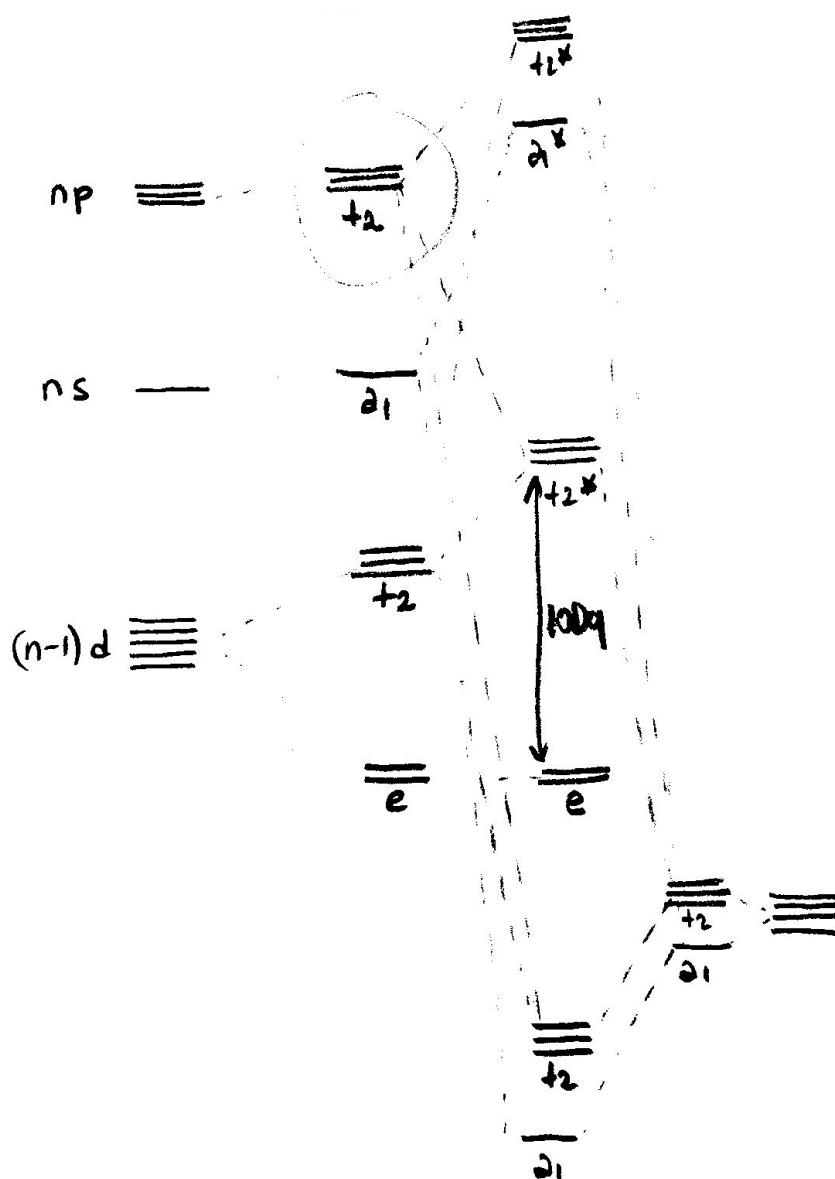




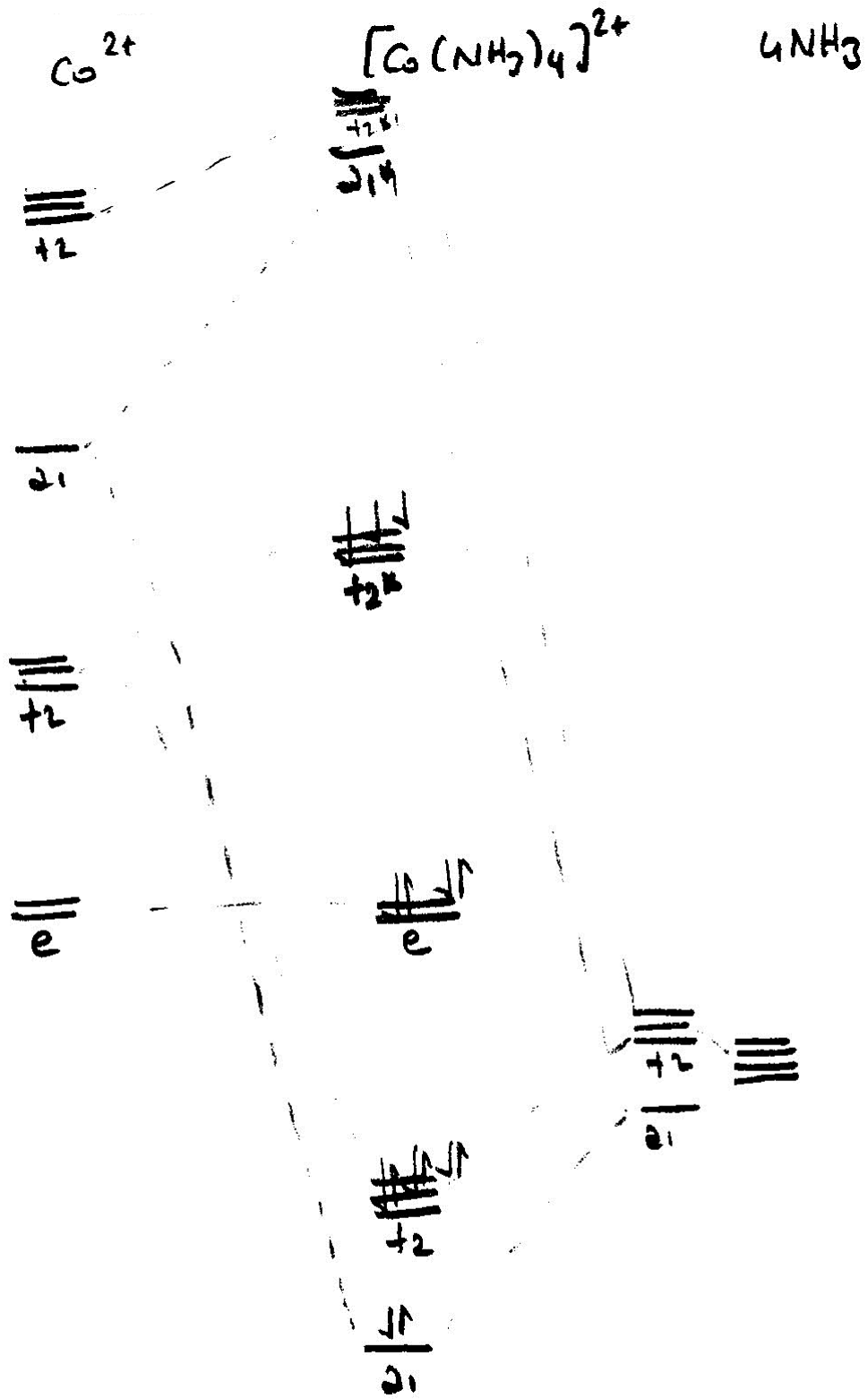
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**TETRAHEDRAL COMPLEXES**

The ligands in the tetrahedral complexes are either the ligand forming only the  $\sigma$ -bond or the  $n$ -donor ligands. The point group of tetrahedral  $ML_4$  complex is  $T_d$ . In the formation of the tetrahedral complex, ligands approach closer to the metal in the direction of the bisector. Therefore,  $t_2$  orbitals form the molecular orbitals. The symmetry of the nine atomic orbitals in the valence shell of the central atom is found in the character table of the  $T_d$  point group as  $a_1$  ( $s$ ),  $t_2$  ( $p_x, p_y, p_z$ ),  $t_2$  ( $d_{xy}, d_{xz}, d_{yz}$ ) and  $e$  ( $d_{x^2-y^2}, d_{z^2}$ ). The symmetry of the ligand group orbitals is  $a_1$  and  $t_2$ .

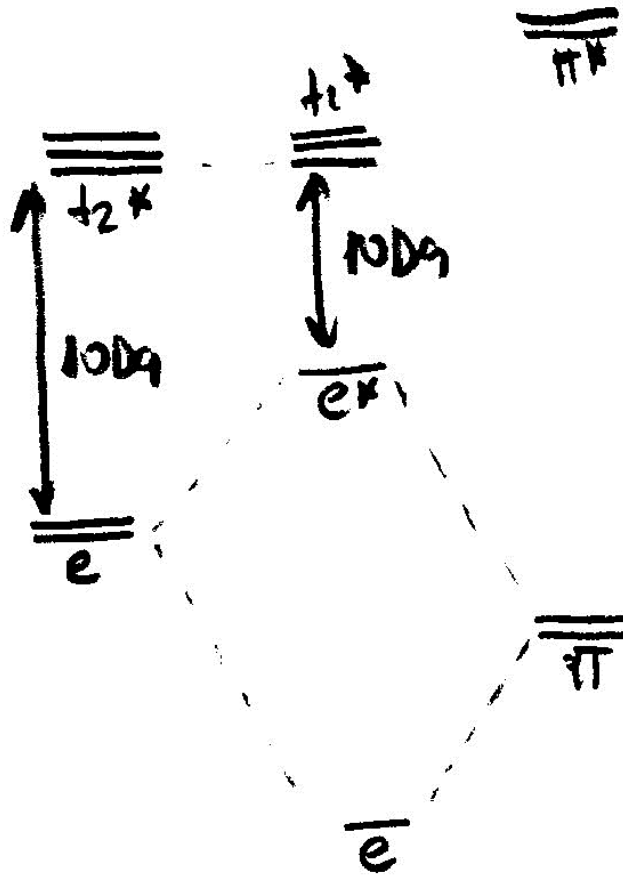


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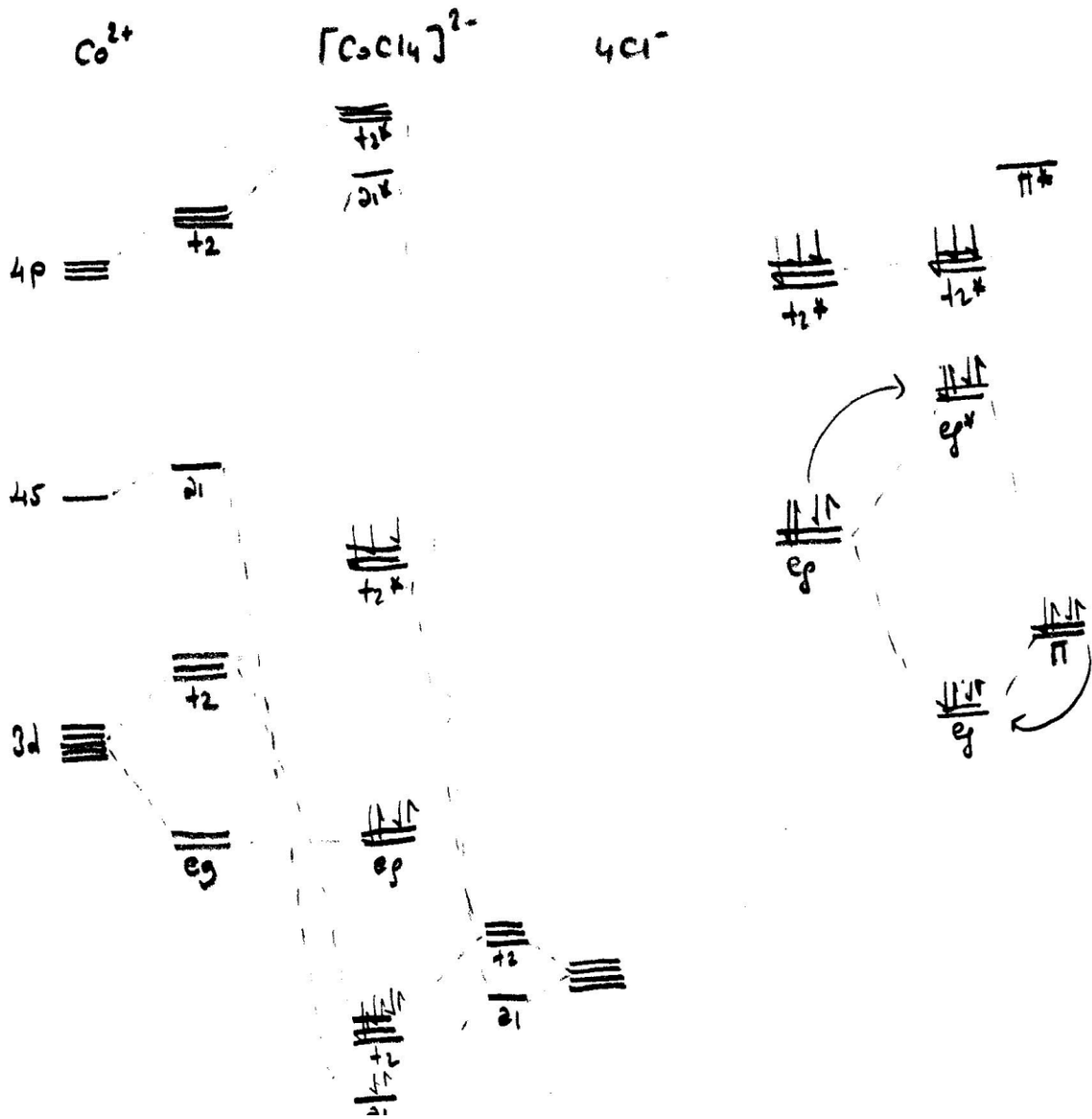


$$(a_1)^2 (t_2)^6 (e)^4 (t_2^*)^3$$

$$BD = \left[ \frac{8-3}{2} \right] / 4 = \frac{5}{8}$$



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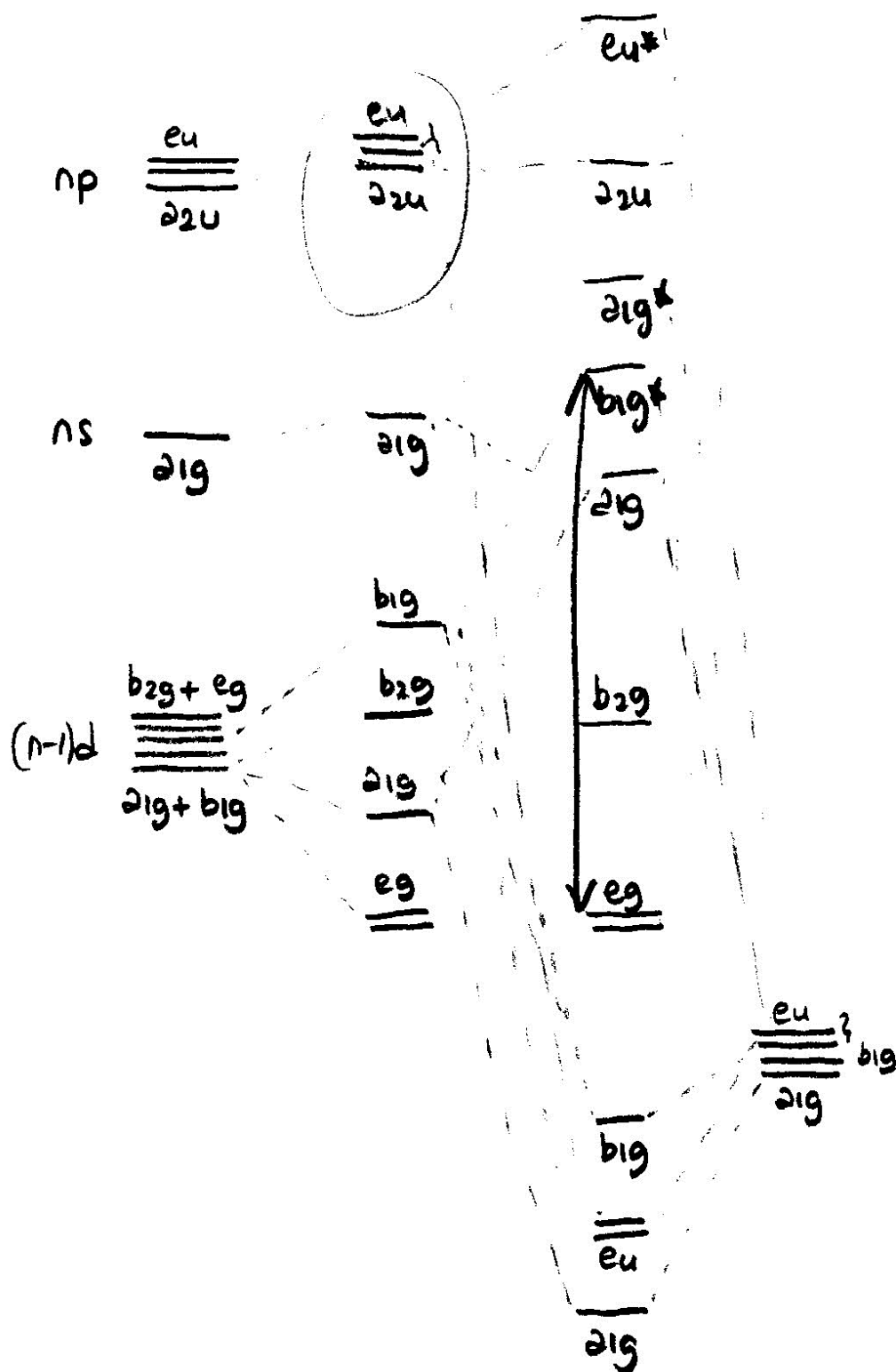


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**SQUARE PLANAR COMPLEXES**

For the metal atom:  $e_g, a_{1g}, b_{2g}, b_{1g}$

For the ligand group orbitals:  $a_{1g}, b_{1g}, e_u$



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<i>Valence Orbitals of Metal</i>	<i>Symmetries</i>	<i><math>\sigma</math>-Ligand group orbital symmetry</i>
<i>s</i>	<i>a<sub>1g</sub></i>	<i>a<sub>1g</sub></i>
<i>d<sub>z<sup>2</sup></sub></i>	<i>a<sub>1g</sub></i>	
<i>d<sub>x<sup>2</sup>-y<sup>2</sup></sub></i>	<i>b<sub>1g</sub></i>	<i>b<sub>1g</sub></i>
<i>p<sub>x</sub>, p<sub>y</sub></i>	<i>e<sub>u</sub></i>	<i>e<sub>u</sub></i>
<i>p<sub>z</sub></i>	<i>a<sub>2u</sub></i>	
<i>d<sub>xy</sub></i>	<i>b<sub>2g</sub></i>	
<i>d<sub>xz</sub>, d<sub>yz</sub></i>	<i>e<sub>g</sub></i>	