## D. Valence Bond Theory (VB) of Complexes <br> Valence Bond Theory is the first theory to explain the electronic properties of complex ions. <br> 1. Octahedral Complexes-metal coordination number $=6$ <br> Problems: <br> $\operatorname{Cr}\left(\mathrm{NH}_{3}\right) 6^{3+}\left(\right.$ in $\left.\left[\mathrm{Cr}\left(\mathrm{NH}_{3}\right)_{6}\right] \mathrm{Cl}_{3}\right)$ <br>  <br> Number of ligands around the central atom 6 <br> Geometry Octahedral <br> Magnetic Properties $\sim$ <br> Electron box diagram <br>  <br> $\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}{ }^{2+}$ (in $\left.\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right] \mathrm{Br}_{2}\right) \quad \mathrm{H}_{2} \mathrm{O}$ <br> Lewis electron dot structure $\mathrm{H}_{2} \mathrm{O}$ <br> $$
\begin{gathered} \mathrm{H}_{2} \mathrm{O} \geq \mathrm{Fe}-\mathrm{CH}_{2} \\ \mathrm{H}_{2} \mathrm{O} \end{gathered} \mathrm{OH}_{2}
$$ <br> Number of ligands around the central atom <br> $\qquad$

Geometry octahedral
Magnetic Properties Paramagneticw/4 unpaired-
electron box diagram

$$
\begin{aligned}
& F e^{2+} \frac{12111}{3 d} \left\lvert\, \frac{4 s}{4 p}-\frac{1}{4}-\begin{array}{c}
\text { Ground } \\
\text { state }
\end{array}\right. \\
& F e^{2+} 121 \frac{11}{3 d} 1
\end{aligned}
$$

$$
\begin{aligned}
& \text { Bonded } \\
& \text { state }
\end{aligned}
$$

## Octahedral Complexes, cont'd



Geometry Octanedenc
Magnetic properities Diamacynetic
Electron box diagram

$$
\begin{aligned}
& F_{e}^{2 t} \text { IL } 1 \frac{1}{3 d} 11 \quad-\frac{1}{4 p} \quad-\frac{1}{3 d}-\text {-state }
\end{aligned}
$$

$$
\begin{aligned}
& \mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right) 6^{2+}\left(\operatorname{in}\left[\mathrm{CO}\left(\mathrm{H}_{2} \mathrm{O}\right) 6\right] \mathrm{Cl} 3\right) \quad \mathrm{H}_{2} \mathrm{O} \\
& \text { Lewis electron dot structure } \mathrm{H}_{2} \mathrm{O} \sim \mathrm{CO}-\mathrm{H}_{2} \mathrm{O} \rightarrow \mathrm{H}_{2} \quad\langle\mathrm{O}<\mathrm{OH}\rangle \\
& \text { Number of ligand around the central atom } \\
& \text { Geometry Octanedeal } \\
& \text { Magnetic properties Para magnetrcu/a } 3 e^{-} \\
& \text {Electron box diagram } \\
& \mathrm{Co}^{2+} 12 \frac{12}{3 d}-1 \\
& \sqrt[4 s]{4 \mathrm{~A}-4 \mathrm{~B}-\mathrm{B}-\begin{array}{l}
\text { Ground } \\
\text { State }
\end{array}} \\
& \mathrm{Co}^{2+} \text { ILILI I I } \\
& 3 d
\end{aligned}
$$

You all have by the end of today
$\mathrm{CO}(\mathrm{CN}) 6^{4-}$ (in $\left.[\mathrm{CO}(\mathrm{CN}) 6] \mathrm{Br} 4\right)$
Lewis electron dot structure


Number of ligands around the central atom 6
Gocmetry Octaneduas

Magnetic Properities
Electron box diagram
$\cos ^{2+} \frac{11}{12} 1-\frac{1}{4 s}-\frac{4 p}{4 p}--\frac{4 d}{}-$ Ground

Excited state

Bonded
$C_{0}{ }^{2+}$ IL U I I

state

$$
3 d
$$


$\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right) 6^{3+}\left(\mathrm{in}\left[\mathrm{Cr}\left(\mathrm{H}_{2} \mathrm{O}\right){ }_{6} \mathrm{JCl}_{3}\right)\right.$
Lewis electron dot structure

$$
\begin{gathered}
\mathrm{H}_{2} \mathrm{O} \\
\mathrm{H}_{2} \mathrm{O} \\
\mathrm{H}_{2} \mathrm{O} \\
1
\end{gathered}
$$

Number of ligands around the central atom 6 $\langle p \circ s t\rangle$
Geometry Octahedral
Magnetic properties para magnetic w/ 3 unpaired eelectron box diagram
$C r^{3+} 7 \frac{1}{3 d-} \quad-\frac{1}{4 s}-\frac{1 p}{4}-\quad$ Ground state
$e r^{3+} 111$


$$
\begin{aligned}
& \text { [Co (en) } 3^{3+} \\
& \text { Number of ligands around the central atom } 3=6 \mathrm{~b} \text { ans } s \text { since } \\
& \text { Geometry Octahedral } \\
& \text { since en = bidentate } \\
& \begin{array}{l}
\text { Magnetic Properties } \\
\text { Energy diagram }
\end{array} \text { en }=\delta F L=\text { low spin complex } \\
& \text { wm } 6 \text { e- } \\
& \mathrm{Co}^{3+} \frac{1 \mathrm{v}}{1} \frac{1}{3 d} \frac{1}{4 s}-\frac{1}{4 p} \text { - Ground State } \\
& \downarrow \text { + Pairing Energy } \\
& c_{0}^{3+} \frac{1 v}{3 d} \frac{7 v}{4 s}-4 p-\text { Excited State } \\
& C_{0}{ }^{3+} \\
& \text { 15 11 76 } \\
& 3 d
\end{aligned}
$$

$$
\begin{aligned}
& \text { 2. Square Planar Complexes - } \mathrm{d}^{\mathrm{B}} \text { metals/Coordination number }=4 \\
& \text { Problems: } \\
& \mathrm{Ni}(\mathrm{CN}) 4^{2-} \\
& \text { Lewis electron dot structure } \\
& \begin{array}{l}
\mathrm{CN} \\
\mathrm{CN} \rightarrow \mathrm{Ni} \rightarrow \mathrm{CN} \\
\mathrm{CN}
\end{array} \\
& \text { Number of ligands around the central atom } \\
& 4
\end{aligned}
$$

> Magnetic Properitios $D$ i a magnet c
> Electron box diagram

$$
\begin{aligned}
& \text { Ni<super>2t ILILIL Excited } \\
& \text { State } \\
& \text { funded } \\
& \mathrm{Ni}{ }^{2+} \\
& \text { gL } \frac{72}{3} \frac{72}{72} \\
& \text { V hybridization } \\
& \text { state } \\
& \text { Lewis electron dot structure } \\
& \text { Number of ligands around the central atom } \\
& 4 \\
& \text { Geometry Square Plaman } \\
& \text { Magnetic Properties Dis mangers } \\
& \text { Electron box diagram }
\end{aligned}
$$

## $\mathrm{Au}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{2}{ }^{-}$

Lewis election dot structure
Number of ligands around the central atom $2=4$ lo ends due to Geometry $\mathrm{C}_{2} \mathrm{O}_{4}^{2-}=$ bidentate
Magnetic Properties: Consider $\mathrm{C}_{2} \mathrm{O}_{4}{ }^{2-}$ as a strong field ligand
Energy diagram

3. Tetrahedral Complexes -Coordination number $=4$
Problems:
$\mathrm{Ni}\left(\mathrm{NH}_{3}\right) 4^{2+}$
Lewis electron dot structure

Number of ligands around the central atom 4
Geometry Tetrahedral
Magnetic Properitien Paramagnet $c c$ w/ 2 unpaired $e^{-}$ electron box diagram
$\mathrm{Ni}^{+2}$
그는 7
$3 d$

$\downarrow$ hybridization

$$
\iint^{N} \frac{\sigma_{2} b \mathrm{cnd}}{2}
$$

$$
\mathrm{Cd}(\mathrm{CN}) 4^{-2}
$$

Lewis electron dot structure

$\langle p o s+\rangle$
Number of ligands around the central atom
Geometry Tetra hedral
Magnetic Properties Diamagnetic
Electron box diagram


$$
\begin{aligned}
& \text { Octahedral, Square planar, and Tetrahedral Complexes } \\
& \text { Problems: } \\
& \mathrm{Co}\left[\left(\mathrm{NH}_{3}\right){ }_{5} \mathrm{H}_{2} \mathrm{O}\right]^{3+} \\
& \text { Number of ligands around the central tam } 6 \\
& \text { magnetic Properties Paramagnets w/ } 4 \text { impaired e- } \\
& \text { Electron box diagram } \\
& \mathrm{Co}^{3+} \\
& \text { 12 } \frac{1}{3 d} 17 \\
& 4-\frac{1}{45}-\frac{4 p}{4 d}--\begin{array}{c}
\text { around } \\
\text { State }
\end{array} \\
& \mathrm{Co}^{3+} \text { 上上 } 1 \frac{1}{3 d} 17 \\
& \text { Lewis electron dot structure } \\
& \text { Geometry } \\
& \text { Octanedual. } \\
& \mathrm{FeCl}_{4}{ }^{-} \\
& \text {Number of ligands around the central atom } 4 \\
& \text { Magnetic Properties Paramagnetic w/ } 5 \text { unpaid e- } \\
& \text { Election box diagram }
\end{aligned}
$$

> Lewis electron dot structure
> Geometry
> Tetra hedral

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    Octahedral,Square planar, and tetrahedral Complexes, cont'd
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    \(\mathrm{PdCl}_{4}{ }^{-2}\)
    Number of ligands around the central atom_ 4
    Magnetic Properties Diamagnetic
Electron box diagram


Magnetic Properities
Diamagnetic
Electron box diagram
$2 n^{2+} \frac{1 L}{3 d} \frac{1 L}{45}-\frac{1 L}{4 p}-\quad$ Ground Stater - nybridization
$2 n^{2+} \frac{7 L}{3 d} \frac{7 L}{T L}$


Lewis electron dot atructurp

Geometry

> Tetrahedral

