D. Valence Bond Theory (VB) of Complexes

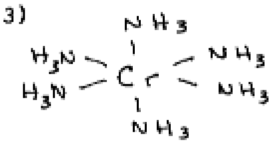
Valence Bond Theory is the first theory to explain the electronic properties of complex ions.

1. Octahedral Complexes-metal coordination number = 6

Problems:

$Cr(NH_3)_6^{3+}$ (in $[Cr(NH_3)_6]Cl_3$)

Lewis electron dot structure

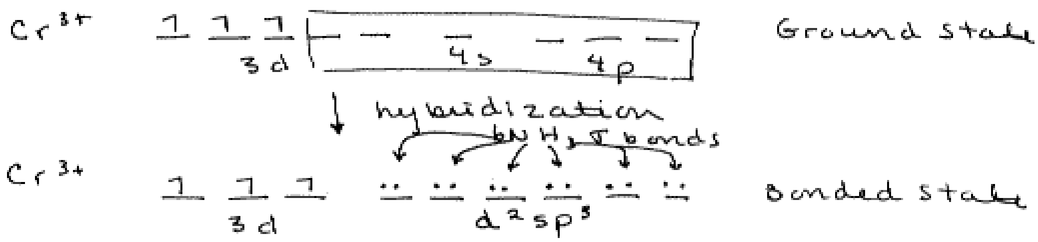


Number of ligands around the central atom 6

Geometry Octahedral

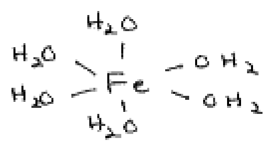
Magnetic Properities

Electron box diagram



$Fe(H_2O)_6^{2+}$ (in $[Fe(H_2O)_6]Br_2$)

Lewis electron dot structure

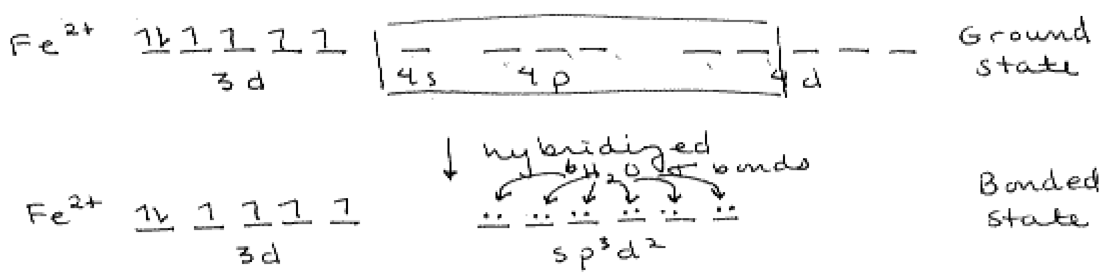


Number of ligands around the central atom 6

Geometry Octahedral

Magnetic Properities Paramagnetic w/ 4 unpaired e-

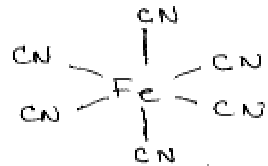
Electron box diagram



Octahedral Complexes, cont'd

$Fe(CN)_6^{4-}$ (in $K_4[Fe(CN)_6]$)

Lewis electron dot structure

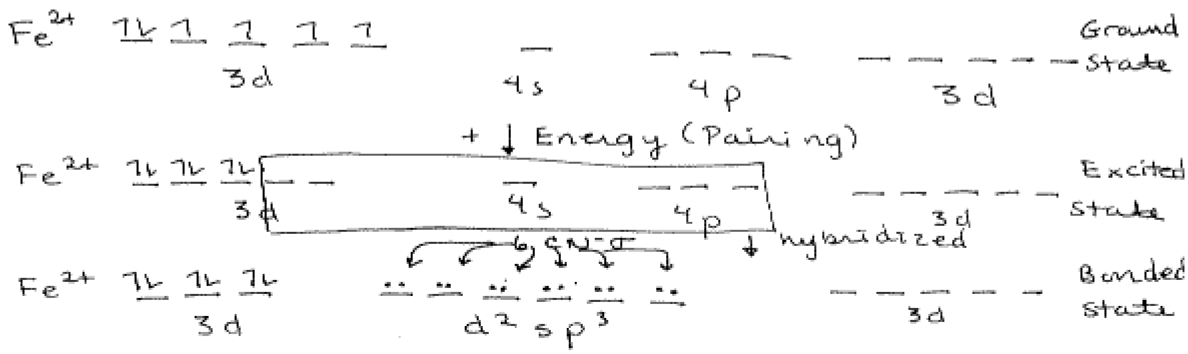


Number of ligands around the central atom 6

Geometry Octahedral

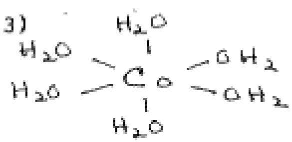
Magnetic Properities Diamagnetic

Electron box diagram



$Co(H_2O)_6^{2+}$ (in $[Co(H_2O)_6]Cl_3$)

Lewis electron dot structure



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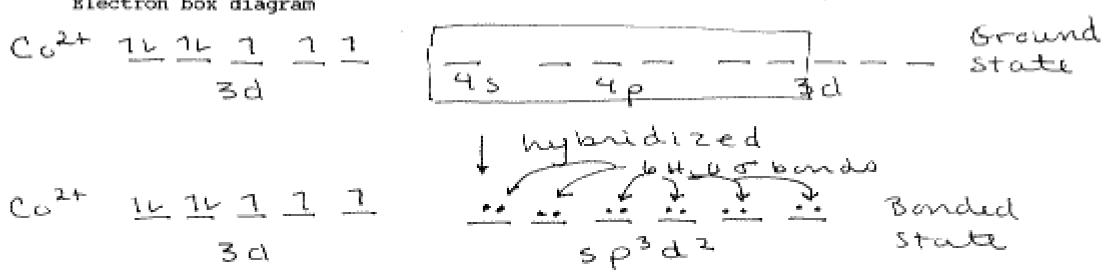
Number of ligands around the central atom 6

Geometry Octahedral

Magnetic Properities Paramagnetic w/ 3 e- unpaired

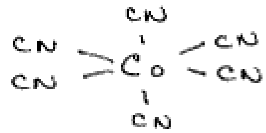
Electron box diagram



You all have by the **end of today**

$Co(CN)_6^{4-}$ (in $[Co(CN)_6]Br_4$)

Lewis electron dot structure

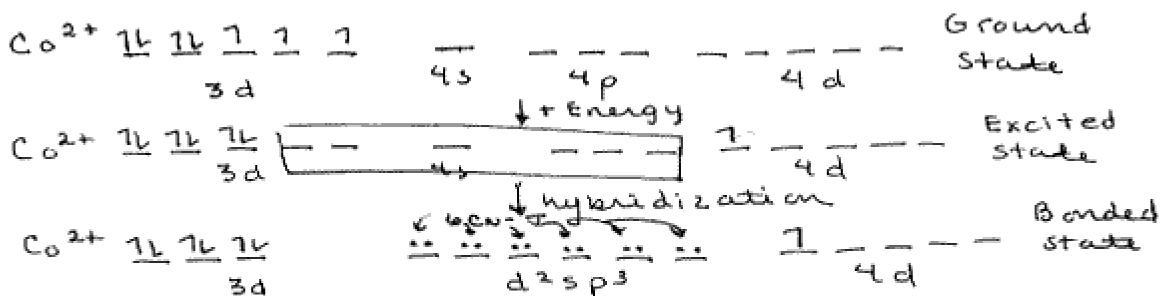


Number of ligands around the central atom 6

Geometry Octahedral

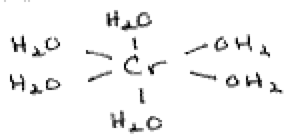
Magnetic Properities

Electron box diagram



$Cr(H_2O)_6^{3+}$ (in $[Cr(H_2O)_6]Cl_3$)

Lewis electron dot structure

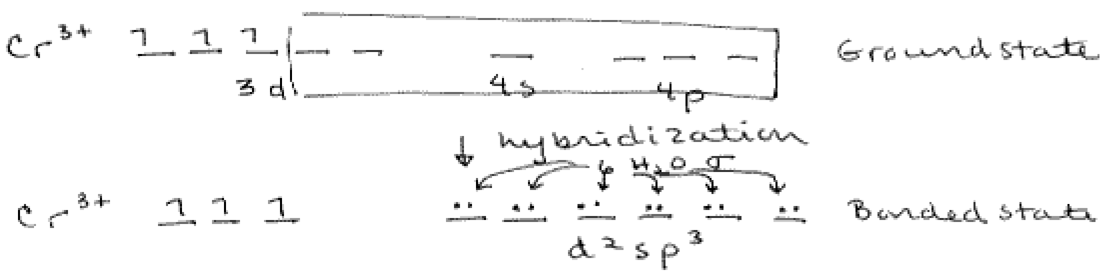


Number of ligands around the central atom 6 <post>

Geometry Octahedral

Magnetic Properities paramagnetic w/ 3 unpaired e-

Electron box diagram



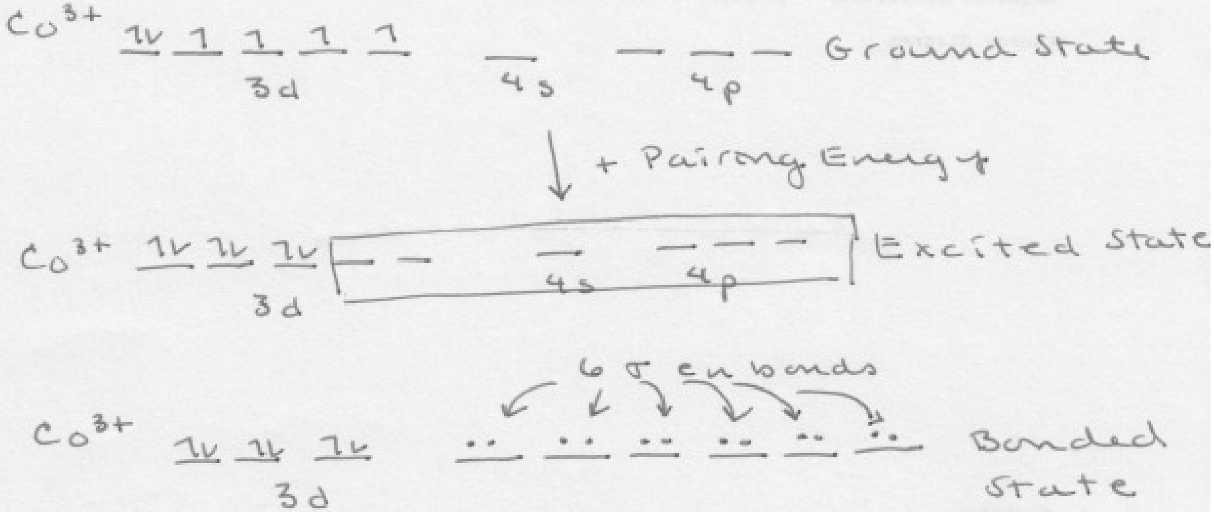
$[Co(en)_3]^{3+}$

Number of ligands around the central atom 3 = 6 bonds since since en = bidentate

Geometry Octahedral

Magnetic Properties en = SFL = low spin complex w/ 6 e-

Energy diagram

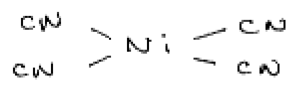


2. Square Planar Complexes - d^8 metals/Coordination number = 4

Problems:

$Ni(CN)_4^{2-}$

Lewis electron dot structure

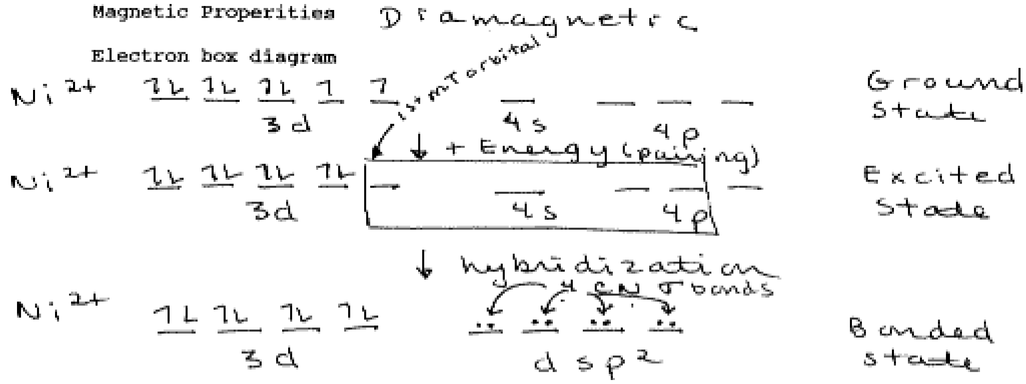


Number of ligands around the central atom ____4____

Geometry Square Planar

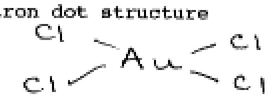
Magnetic Properities Diamagnetic

Electron box diagram



$Au^{3+}Cl_4^{4-}$ $AuCl_4^-$

Lewis electron dot structure



Number of ligands around the central atom ____4____

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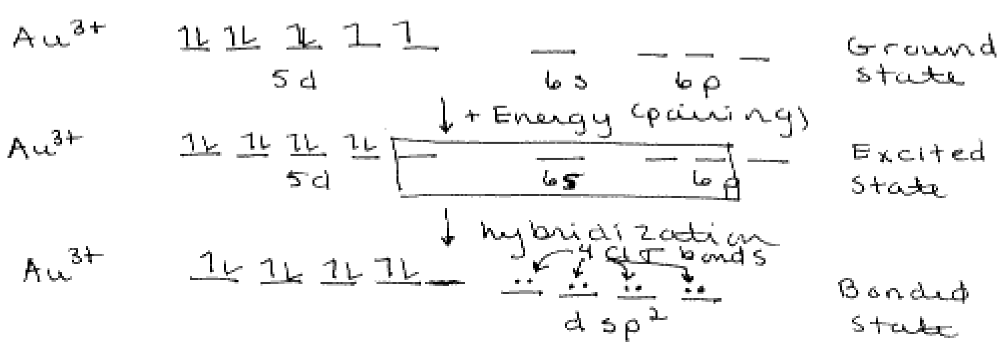
Geometry Square Planar

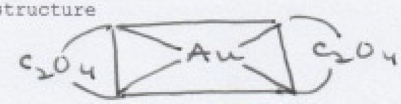
Magnetic Properities Diamagnetic

Electron box diagram



$Au(C_2O_4)_2^-$

Lewis electron dot structure



Number of ligands around the central atom 2 = 4 bonds due to $C_2O_4^{2-}$ = bidentate

Geometry

Magnetic Properties: Consider $C_2O_4^{2-}$ as a strong field ligand

Energy diagram

Au^{3+} ⇅ ⇅ ⇅ ↑ ↑ (3d) — (4s) — — — (4p) Ground State

↓ + Pairing Energy

Au^{3+} ⇅ ⇅ ⇅ ⇅ (3d) $\boxed{—\ (4s)\ —\ —\ (4p)}$ — Excited State

4 σ $C_2O_4^{2-}$ bonds

Au^{3+} ⇅ ⇅ ⇅ ⇅ (3d) : : : : (dsp^2) Bonded state

↓

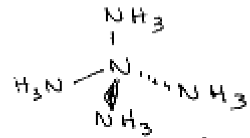
Aha! dsp^2 ∴ square planar!

3. Tetrahedral Complexes - Coordination number = 4

Problems:

$Ni(NH_3)_4^{2+}$

Lewis electron dot structure



Number of ligands around the central atom 4

Geometry Tetrahedral

Magnetic Properities Paramagnetic w/ 2 unpaired e-

Electron box diagram

1st MT orbital

Ni^{+2} ↑↓ ↑↓ ↑↓ ↑ ↑ (3d) | _ (4s) _ _ _ (4p) | Ground state

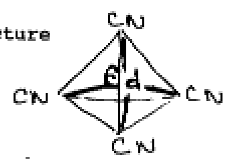
↓ hybridization

NH_3 σ bond

Ni^{2+} ↑↓ ↑↓ ↑↓ ↑ ↑ (3d) .. .. (sp^3) Bonded state

$Cd(CN)_4^{-2}$

Lewis electron dot structure



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Number of ligands around the central atom 4

Geometry Tetrahedral

Magnetic Properities Diamagnetic

Electron box diagram

Cd^{2+} ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ (3d) | _ (4s) _ _ _ (4p) | Ground state

↓ hybridization

CN σ bonds

Cd^{2+} ↑↓ ↑↓ ↑↓ ↑↓ ↑↓ (3d) ↑↓ ↑↓ ↑↓ ↑↓ (sp^3) Bonded state

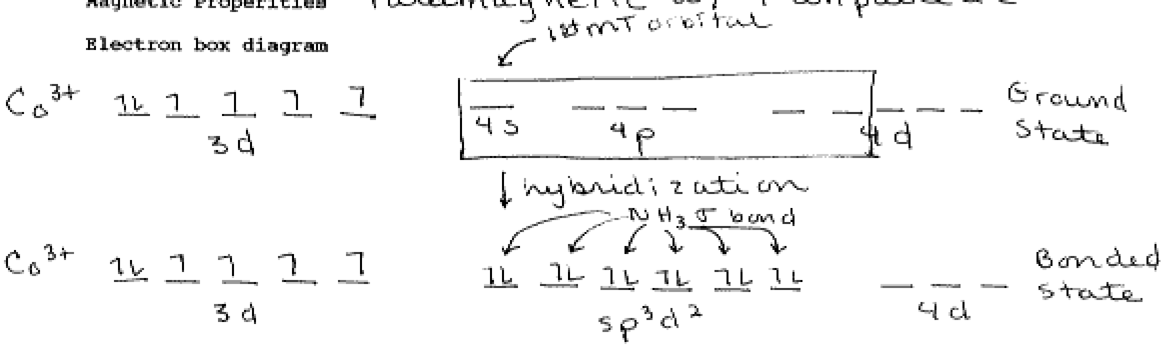
Octahedral, Square Planar, and Tetrahedral Complexes
Problems:

$Co[(NH_3)_5H_2O]^{3+}$

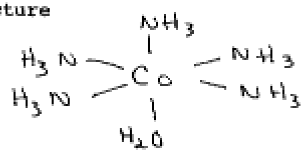
Number of ligands around the central atom 6

Magnetic Properities Paramagnetic w/ 4 unpaired e-

Electron box diagram



Lewis electron dot structure



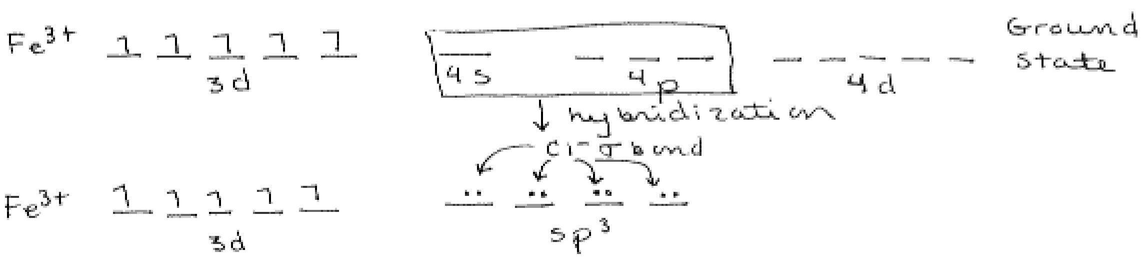
Geometry Octahedral

$FeCl_4^-$

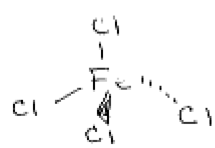
Number of ligands around the central atom 4

Magnetic Properities Paramagnetic w/ 5 unpaired e-

Electron box diagram



Lewis electron dot structure



Geometry Tetrahedral

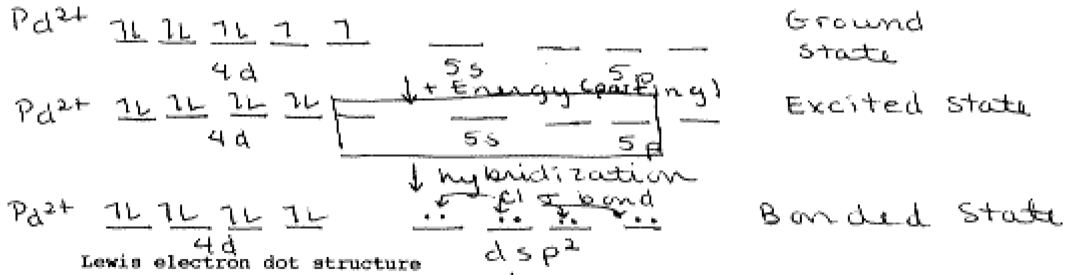
Octahedral, Square Planar, and tetrahedral Complexes, cont'd

$PdCl_4^{-2}$

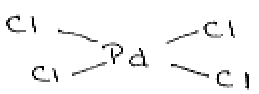
Number of ligands around the central atom 4

Magnetic Properities Diamagnetic

Electron box diagram



Lewis electron dot structure



Geometry Square Planar

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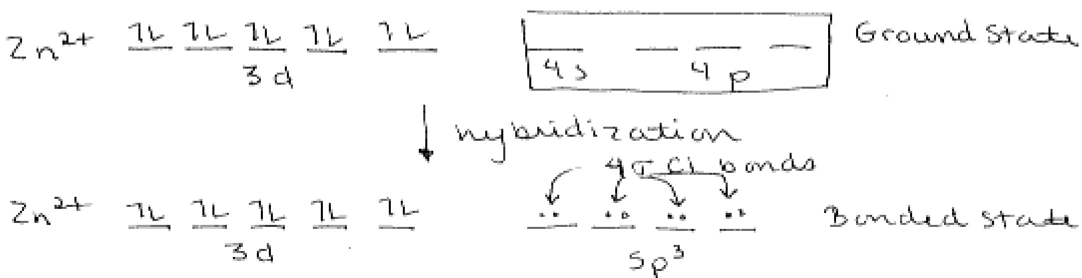
$ZnCl_4^{2-}$

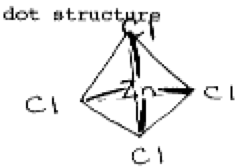
Number of ligands around the central atom 4

Magnetic Properities Diamagnetic

Electron box diagram



Lewis electron dot structure



Geometry Tetrahedral