**In-Class Activity: Using Correlation to Derive a Ligand-Field-Splitting Diagram**

Five-coordinate transition metal complexes exhibit two common geometries, trigonal bipyramidal and square pyramidal. Please answer the following questions about the electronic structures of complexes with these geometries.

1. Vanadium often forms five-coordinate complexes with π-donor ligands that adopt square pyramidal geometry. Using the octahedral ligand-field splitting as a starting point, follow the steps below to determine a qualitative ligand-field splitting diagram for V(O)(NH3)4+.

Please fill in the tables to indicate how each step affects the symmetry, energy, and bonding nature of each *d* orbital.



|  |  |  |
| --- | --- | --- |
| **V(NH3)63+ starting complex** | | |
| *d* orbital | Symmetry Label | σ/π/nb/σ\*/π\* |
| *z*2 |  |  |
| *xz* |  |  |
| *yz* |  |  |
| *xy* |  |  |
| *x*2–*y*2 |  |  |

|  |  |  |  |
| --- | --- | --- | --- |
| **Step (a) – Remove axial ligand** | | | |
| *d* orbital | Symmetry Label | Energy ↑, ↓, or no change | σ/π/nb/σ\*/π\* |
| *z*2 |  |  |  |
| *xz* |  |  |  |
| *yz* |  |  |  |
| *xy* |  |  |  |
| *x*2–*y*2 |  |  |  |

|  |  |  |  |
| --- | --- | --- | --- |
| **Step (b) – Distort equatorial ligands out of plane** | | | |
| *d* orbital | Symmetry Label | Energy ↑, ↓, or no change | σ/π/nb/σ\*/π\* |
| *z*2 |  |  |  |
| *xz* |  |  |  |
| *yz* |  |  |  |
| *xy* |  |  |  |
| *x*2–*y*2 |  |  |  |

|  |  |  |  |
| --- | --- | --- | --- |
| **Step (c) – Substitute O2– for NH3** | | | |
| *d* orbital | Symmetry Label | Energy ↑, ↓, or no change | σ/π/nb/σ\*/π\* |
| *z*2 |  |  |  |
| *xz* |  |  |  |
| *yz* |  |  |  |
| *xy* |  |  |  |
| *x*2–*y*2 |  |  |  |

1. The final vanadium oxo complex, V(O)(NH3)4+, has a qualitative ligand-field splitting diagram as shown below. Provide symmetry labels and associated *d* orbitals for each orbital displayed.



1. The vanadium oxo complex in part (a) is shown as a V=O double bond. Is this formulation correct based on your MO diagram? If not, what bond order is more appropriate?
2. Predict a spin state (*S* value) and spin-only magnetic moment (μeff, in Bohr magnetons) for the first and last complexes in the series above (V(NH3)63+ and V(O)(NH3)4+)? Explain if there is any ambiguity.
3. Vanadium oxo complexes such as the one described above have a strong preference for square pyramidal over trigonal bipyramidal geometries. Using what you know about ligand-field theory, provide a rationale for why a trigonal bipyramidal geometry (shown below) might be unfavorable for V(O)(NH3)4+.

