Octahedral complexes with between 4 and 7 d electrons can be either high-spin or low-spin depending on the size of Δ. When the ligand field splitting has an intermediate value such that the two states have similar energies, then the two states can coexist in measurable amounts at equilibrium. Many "crossover" systems of this type have been studied, particularly for iron complexes.

The change in spin state is a transition from a low spin (LS) ground state electron configuration to a high spin (HS) ground state electron configuration of the metal’s d atomic orbitals (AOs), or vice versa. The magnitude of the ligand field splitting along with the pairing energy of the complex determines whether it will have a LS or HS electron configuration. A LS state occurs because the ligand field splitting (Δ) is greater than the pairing energy of the complex (which is an unfavorable process).

Figure 1: Diagram illustrating the dependence of the HS or LS state on Δ of the octahedral ligand field splitting and the corresponding electron configuration.

Figure 1 is a simplified illustration of the metal’s d orbital splitting in the presence of an octahedral ligand field. A large splitting between the t_{2g} and e_{g} AOs requires a substantial amount of energy for the electrons to overcome the energy gap (Δ) to comply with Hund’s Rule. Therefore, electrons will fill the lower energy t_{2g} orbitals completely before populating the higher energy e_{g} orbitals. Conversely, a HS state occurs with weaker ligand fields and smaller orbital splitting. In this case the energy required to populate the higher levels is substantially less than the pairing energy and the electrons fill the orbitals according to Hund’s Rule by populating the higher energy orbitals before pairing with electrons in the lower lying orbitals. An example of a metal ion that can exist in either a LS or HS state is Fe^{3+} in an octahedral ligand field. Depending on the ligands that are coordinated to this complex the Fe^{3+} can attain a LS or a HS state, as in Figure 1.
At the higher temperature the ground state is $^{5}T_{2g}$ while at low temperatures it changes to $^{1}A_{1g}$. The changeover is found at about 174 K. In solution studies, it is possible to calculate the heat of conversion from the one isomer to the other.

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