

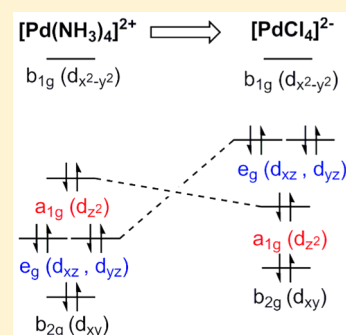
Transition Metal d-Orbital Splitting Diagrams: An Updated Educational Resource for Square Planar Transition Metal Complexes

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S Supporting Information

ABSTRACT: The presentation of d-orbital splitting diagrams for square planar transition metal complexes in textbooks and educational materials is often inconsistent and therefore confusing for students. Here we provide a concise summary of the key features of orbital splitting diagrams for square planar complexes, which we propose may be used as an updated reference in chemical education.



KEYWORDS: General Public, Upper Division Undergraduate, Inorganic Chemistry, Textbooks, Crystal Field/Ligand Field Theory, MO Theory, Transition Elements

INTRODUCTION

The influence of ligands on the energetic ordering of transition metal d-orbitals is of great fundamental importance in organometallic and inorganic chemistry. It allows one to predict and explain the structure, reactivity, spectroscopic transitions, and magnetic properties of transition metal complexes. Therefore, d-orbital splitting diagrams are an essential part of chemical education, so that students develop a proper understanding of how different types of ligand environments influence the properties of transition metal complexes.^{1–4} To our surprise we have found that educational materials typically used for introductory organometallic and inorganic chemistry courses do not adequately address d-orbital splitting diagrams for square planar complexes. But due to the fact that square planar transition metal complexes are ubiquitous in modern organometallic chemistry and catalysis, it is important to provide students with an appropriate understanding of their electronic structure. Here we provide a concise summary of d-orbital splitting diagrams for square planar transition metal complexes, which we propose may be used as an updated reference in chemical education.

Introductory courses typically present d-orbital splitting diagrams to students using a crystal field theory (CFT) analysis for octahedral (O_h) and tetrahedral (T_d) geometries, and the archetypal splitting diagrams for these geometries are shown in Figure 1.^{2,5–8} From an educational perspective, it is convenient that the CFT-derived orbital splitting diagrams for O_h and T_d complexes are generally representative for complexes in these coordination environments. A higher-level analysis, such as one that considers π -donor/acceptor interactions with ligands, does

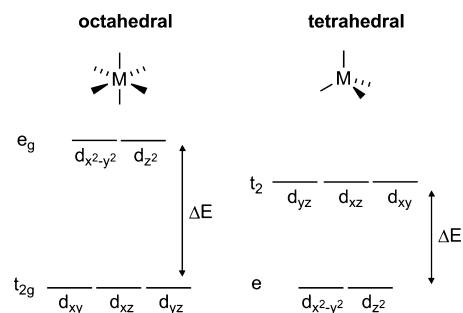


Figure 1. Archetypal d-orbital splitting diagrams for octahedral and tetrahedral transition metal complexes. Consideration of ligand σ -donor and π -donor/acceptor abilities affects the magnitude of the orbital splitting (ΔE), but not the relative ordering of the metal-based orbitals.

not typically change the qualitative ordering of the orbital sets but only the magnitude of the orbital splitting (ΔE). On the other hand, it has long been recognized that CFT cannot provide such a “representative” orbital splitting diagram for square planar (D_{4h}) complexes.^{9–14} The relative ordering of the orbitals can vary depending on the ligand field, and this simple fact has led to an unfortunate consequence: many textbooks in the field erroneously present a single orbital splitting diagram for square planar complexes as being general, or avoid the subject altogether. And while the factors that affect orbital splitting for square planar complexes are well-understood thanks to decades of spectroscopic and computational

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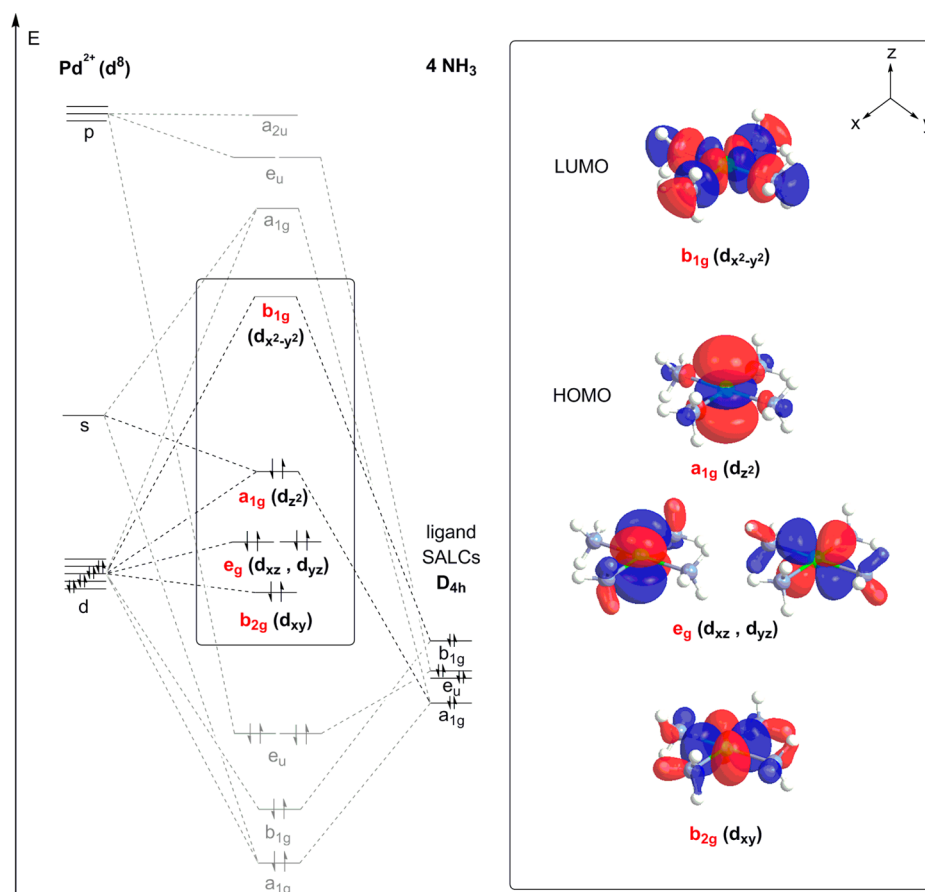


Figure 2. Qualitative molecular orbital (MO) diagram for square planar complexes with purely σ -donor ligands (based on $[\text{Pd}(\text{NH}_3)_4]^{2+}$ as a representative example). The orbitals with mainly metal d-orbital parentage are highlighted and visualized, with the specified metal d-orbital given in parentheses. The ligand orbitals participating in σ -bonding are combined to symmetry adapted linear combinations (SALCs) within the point group D_{4h} . The relative energy levels of the metal and ligand atomic orbitals are arbitrarily chosen based on Pauling electronegativity values.

studies,^{15–33} this information is typically not incorporated into educational resources that are accessible to students. Our goal here is therefore to outline a few general trends that students can use to understand how orbital splitting for square planar complexes is affected by different types of ligands.

d-Orbital Splitting for Pure σ -Donor Ligands

For square planar complexes with ligands that function only as σ -donors (with no π -donor or -acceptor character), a representative molecular orbital (MO) diagram is shown in Figure 2, as calculated for $[\text{Pd}(\text{NH}_3)_4]^{2+}$.³⁴ A key feature of d-orbital splitting for all square planar complexes is that the b_{1g} orbital (derived from the metal $d_{x^2-y^2}$ orbital) is driven significantly higher in energy than the rest of the d-orbital based MOs, due to strong metal–ligand antibonding interactions in the xy plane.¹ The b_{1g} orbital of metal $d_{x^2-y^2}$ orbital parentage is the lowest unoccupied molecular orbital (LUMO) for some square planar complexes, but is not necessarily the LUMO in all cases.^{35–39} The remaining d-orbital based MOs are typically close in energy, and their relative ordering depends on the nature of the ligands. For complexes with purely σ -donor ligands, the a_{1g} orbital (of metal d_z^2 parentage) is expected to be the highest occupied molecular orbital (HOMO). This observation is based on the fact that the torus-shaped lobe of the a_{1g} orbital participates in minor metal–ligand antibonding interactions in the xy plane.¹ The MOs with metal d_{xy} , d_{xz} , and d_{yz} orbital parentage are nonbonding and often presented as degenerate because there

is no symmetry match with the ligand orbital set.^{1,2,4,40} Splitting of these orbitals into two sets (e_g and b_{2g}) is required by group theory considerations according to the irreducible representations of the D_{4h} point group, but the factors that determine the relative ordering of the e_g and b_{2g} orbitals in a complex with purely σ -donor ligands are beyond the scope of this discussion.^{2,11}

d-Orbital Splitting Trends for Ligands with π -Character

Typically the effect of ligands with π -donor or -acceptor character on d-orbital splitting is discussed for octahedral complexes in educational materials, since it is the easiest case and it allows one to rationalize the spectrochemical series.^{5,41} For octahedral complexes, the ordering of the MOs is qualitatively the same regardless of the type of ligands; only the extent of the splitting between the t_{2g} -orbital set (HOMO) and the e_g -orbital set (LUMO) is influenced (ΔE ; Figure 1). However, for square planar complexes, considering the π -character of the ligands can have a significant effect on the energetic ordering of the MOs.^{2,4,40}

The splitting of the d-orbital based MOs for square planar complexes with π -acceptor ligands such as cyanide is qualitatively the same as for pure σ -donor ligands (Figure 3, left).^{27,42} However, the energetic ordering is perturbed by π -donating ligands such as chloride (Figure 3, right).⁹ For square planar complexes with strongly π -donating ligands, the HOMO is the degenerate e_g -orbitals of metal d_{xy} and d_{yz} parentage, in large part due to destabilization from π -antibonding inter-

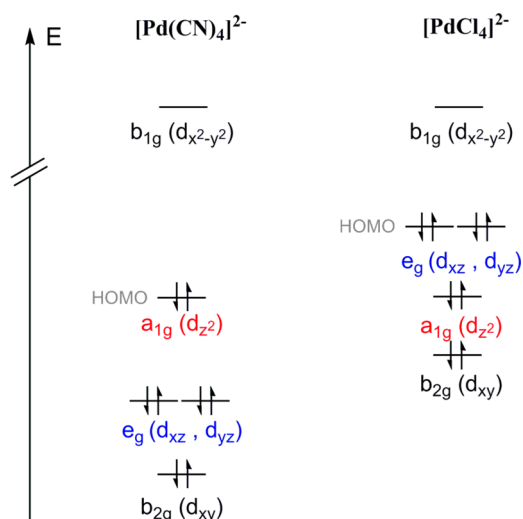


Figure 3. Truncated MO diagrams for square planar complexes with ligands that have π -acceptor character (e.g., $[\text{Pd}(\text{CN})_4]^{2-}$, left) and π -donor character (e.g., $[\text{PdCl}_4]^{2-}$, right). Ligands with π -donor character are known to significantly perturb the ordering of the metal-based MOs in square planar complexes.

actions with the lone pairs of the ligands. In contrast, the a_{1g} orbital with metal d_{z^2} -orbital parentage is energetically stabilized, due to the weak σ -donating properties of ligands such as chloride, and is no longer the HOMO of the complex. The orbital splitting for complexes with π -donor ligands, such as $[\text{PdCl}_4]^{2-}$, has been a topic of particular confusion because the calculated and the spectroscopically determined orbital splitting diagrams differ in some cases.²⁵ These differences can be understood based on changes in relative orbital ordering between the electronic excited states and the ground state,^{43–46} and the calculated diagram for $[\text{PdCl}_4]^{2-}$ shown in Figure 3 best represents the electronic ground state of the complex.⁴⁷ The relative energies of the b_{2g} and a_{1g} orbitals can vary between different complexes, and may be reversed as compared to the example diagram shown here for $[\text{PdCl}_4]^{2-}$.

CONCLUSIONS

In summary, we have attempted here to provide an accessible educational reference regarding d-orbital splitting diagrams for square planar transition metal complexes. While it is incorrect to provide one “general” orbital splitting diagram for square planar complexes, we propose that the orbital diagrams presented here can be used by students and educators to establish guidelines for orbital splitting based on various ligand types. In particular, the effect of π -donor ligands on the frontier MOs of square planar complexes (Figure 3) is a critical point that is well-understood but has been neglected in textbooks to date. Because the energy and symmetry of the frontier MOs can impact the reactivity of a transition metal complex, it is important for students to understand such trends. Of course, no single MO diagram can be taken as representative of all complexes of a given geometry, but the available experimental and computational data supports that the handful of simplified orbital diagrams shown in this essay are consistent with overall trends for square planar complexes. We hope that the analysis presented here will be valuable as an educational resource, and will allow students in the field to begin developing a more advanced understanding of the electronic structure of transition metal complexes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00542.

DFT calculation details (PDF)

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Notes

The authors declare no competing financial interest.

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