



## 7.1 Bonding in Coordination Compounds

### Bonding in Coordination Compounds

This chapter is devoted to bonding theories for coordination compounds. Let us first think about, what a good theory should be able to do in general. The answer is, that it should be able to make many correct explanations for experimental observations based on a few, sensible, assumptions. In addition, it should be able to predict experimental observations. The more the theory can explain and predict, and the fewer the necessary assumptions, the better the theory. What does this mean for a bonding theory? What would a good bonding theory for coordination compounds be able to do? It should certainly be able to explain and predict the number of bonds and the shape of a molecule. In addition, it should be able to explain the magnetism of molecules, in particular dia- and paramagnetism. Remember, a molecule is diamagnetic when it has no unpaired electrons. It is paramagnetic when there are unpaired electrons. A diamagnetic molecule is repelled by an external magnetic field. A paramagnetic molecule is attracted by an external magnetic field. It should further be able to explain the stability and reactivity of complexes, as well as the optical properties of complexes. Optical properties of compounds are linked to bonding because they are related to electronic states.

### Valence Bond Theory

There are essentially three bonding concepts that are used to describe the bonding in coordination compounds. The first one is the valence bond theory. The valence bond concept was introduced by Linus Pauling in 1931 to explain covalent bonding in molecules of main group elements.

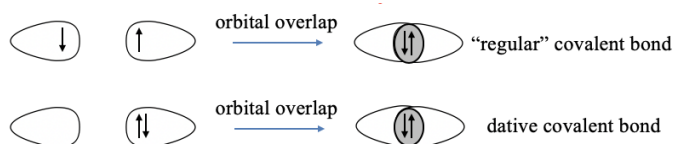


Figure 7.1.1 Electron sharing and valence bond theory

The basic idea is to overlap half-filled valence orbitals to form covalent bonds in which the two electrons are shared between the bonding partners (Fig. 7.1.1). These orbitals can either be atomic orbitals, or hybridized atomic orbitals. The concept works very well to explain the shapes of molecules of main group elements. The valence bond concept in its original form assumes that each bonding partner contributes one electron to the covalent bond. This is not consistent with the dative bonding in coordination compounds where it is assumed that one partner donates an electron pair and the other partner accepts it. To adapt valence bond theory to suit coordination compounds, Pauling suggested that a dative bond is formed via the overlap of a full valence orbital of the donor and an empty valence orbital of the acceptor. We will see that this concept can explain the shapes of coordination compounds in some cases, but overall it does not work very well. We will also see that valence bond theory can explain magnetism in some cases, but also here the valence bond theory has significant deficits. By its nature, valence bond theory cannot explain optical properties. Overall, valence bond theory is far more suitable for main group element molecules compared to transition metal complexes.

### Crystal Field Theory

The second major theory is the crystal field theory. It is actually not a bonding theory because it is based on repulsive electrostatic interactions. It was originally developed to explain color in ionic crystals. Later, it was found that it can also explain colors in molecular coordination compounds, and is suitable to explain shapes and magnetism of complexes. However, because it is based on repulsive electrostatic interactions it cannot actually explain what holds the atoms in a molecule together. However, the crystal field theory is quite simple and convenient to use, and there is a lot of practicality to it.

### Ligand Field Theory

The third theory is the ligand field theory. It is the most powerful theory, but also the most complicated one. Basically, it is molecular orbital theory applied to coordination compounds. It can make detailed statements about the number of bonds and shapes of molecules, and can explain the magnetism and optical properties of coordination compounds.

## Valence Bond Theory for Coordination Compounds

### Octahedral Complexes



Let us have a closer look at the valence bond theory, and assess valence bond theory for complexes by a number of examples.

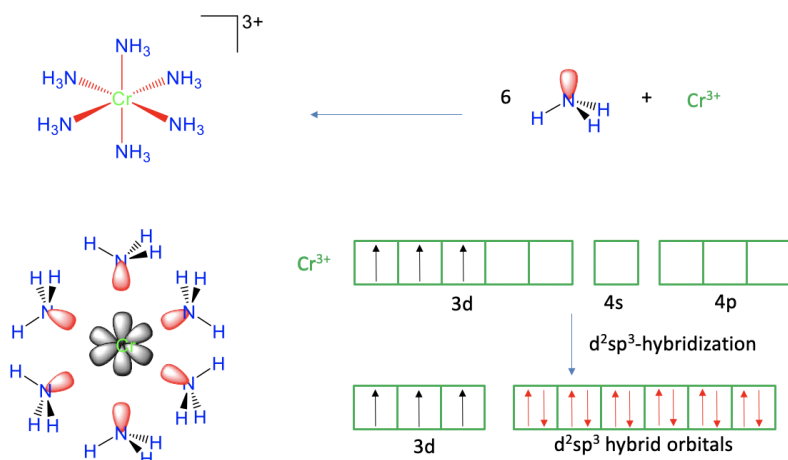


Figure 7.1.2 Valence bond theory

applied to the hexaammine chromium (3+) cation

The first example is the hexaammine chromium (3+) cation (Fig. 7.1.2). From experiment we know that it has an octahedral shape, with six dative Cr-N bonds. Can valence bond theory explain the six bonds and the octahedral shape satisfactorily? In order to explain the six dative Cr-N bonds we would need to overlap six empty chromium valence orbitals with six filled valence orbitals of N. We can see that the six ammine ligands have one electron lone pair each that can serve as the valence orbitals. Does chromium have six empty valence orbitals? In order to assess this, we first need to know the oxidation state of the chromium. It is +3 because the ligands are all neutral when the bonds are cleaved heteroleptically, and the complex cation has a 3+ charge. Therefore, the chromium is a  $\text{Cr}^{3+}$  cation.

Next, we need to know the electron configuration of the  $\text{Cr}^{3+}$ . A neutral Cr atom has the electron configuration  $4s^1 3d^5$ . When a transition metal loses electrons to form a cation, it always loses its two valence electrons first, and then its d electrons. For chromium this means that we must remove the one 4s electron, and two of the five 3d-electrons. The three remaining 3d electrons are expected to be spin up in three different d orbitals according to Hund's rule. How many empty valence orbitals remain? These would be two 3d and the 4s orbitals. In addition, it would also be justified to consider the three 4p orbitals as valence orbitals because the 4p orbitals are energetically only slightly higher than the 4s orbital. That means that we would have the six valence orbitals that we would need to explain the six bonds. There is, however, a complication. The six bonds in the complex are not distinguishable, but the six valence orbitals in the  $\text{Cr}^{3+}$  ion are distinguishable, for example, the 3d orbitals have different shape and energy than the 4s orbital, which is different from the 4p orbitals. Therefore, if we overlapped these orbitals with the electron lone pairs at N, the bonds would not be equivalent, or indistinguishable. We would have difficulty to explain the highly symmetric octahedral shape of the molecule. To go around this issue, valence bond theory uses the concept of hybridization. In this concept we mathematically mix the wave functions of the valence orbitals to form hybridized orbitals. In our example we would mix the two empty d-orbitals, the 4s orbital, and the three 4p orbitals to form six so-called  $d^2sp^3$  hybridized orbitals. They have the same shape and size, and their lobes point toward the corners of an octahedron. Therefore, we can now create overlap between these six orbitals, and the six electron lone pairs at N to form six equivalent, indistinguishable Cr-N bonds. We conclude that we have now satisfactorily explained the bonding and the shape of the complex.

Can we also explain its magnetism? From experiment we know that the complex is paramagnetic, and that there are three unpaired electrons. Does valence bond theory predict the same? Yes, it does. There are three unpaired electrons in the three half-filled d-orbitals.

### Tetrahedral Complexes

Our next example is a tetrahedral complex, the tetrahydroxo zincate (2-) complex anion, Fig. 7.1.3.

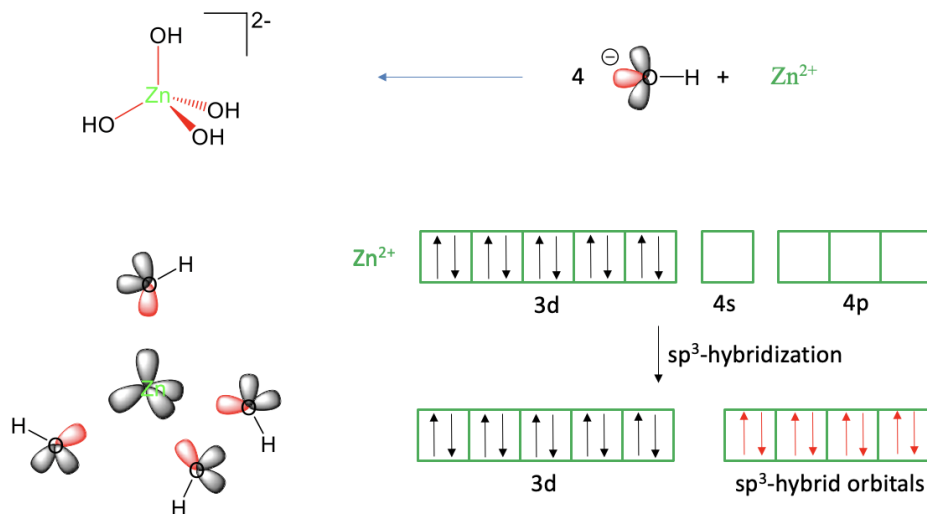


Figure 7.1.3 Valence bond theory applied to the tetrahydroxo zincate (2-) complex.

When viewing it as a Lewis-acid base complex with dative bonds it can be thought as an adduct of a  $\text{Zn}^{2+}$  and four hydroxide anions. One of the three electron lone pairs at the hydroxide ions would donate its electrons into empty Zn valence orbitals. That means we would need overall four empty Zn valence orbitals to explain the four Zn-O bonds. A neutral zinc atom has the electron configuration  $4s^2 3d^{10}$ . We can derive this from the fact that zinc is in group 12 of period 4 in the periodic table. A  $\text{Zn}^{2+}$  ion has two electrons less. Because we must remove s electrons before we remove d electrons, the  $\text{Zn}^{2+}$  has the electron configuration  $3d^{10}$ . Like in the previous example we can justifiably consider the 4p orbitals as additional valence orbitals. We can see that we have four empty orbitals available to make the four bonds, namely the 4s and the 4p orbitals, but these orbitals are not equivalent, and do not have the correct orientation to explain the tetrahedral shape of the complex. There is a  $90^\circ$  angle between the p-orbitals which is smaller than the  $109.5^\circ$  tetrahedral bond angle in the molecule. However, we can solve this problem by hybridizing the 4s and the three 4p orbitals to form four  $\text{sp}^3$ -hybridized orbitals. These hybrid orbitals have the property that their lobes point toward the corners of a tetrahedron. Thus, they are suitable to explain the tetrahedral shape of the molecule. We can place the ligands around the  $\text{Zn}^{2+}$  ion and approach the ligands on the bond axes to create orbital overlap between the empty  $\text{sp}^3$ -hybridized orbitals and one electron lone pair at the oxygen atom. This produces the tetrahedral tetrahydroxo zincate (2-) anion.

Can we also explain the magnetism of the molecule? What magnetism would valence bond theory predict? We can see that there are no unpaired electrons in any of the metal valence orbitals. Thus, the complex should be diamagnetic. This is also what we find experimentally. Thus, valence bond theory is able to explain the magnetism of this complex anion.

### Square Planar Complex

Now let us see if the valence bond theory can also explain a square planar complex such as tetracyanonickelate (2-).

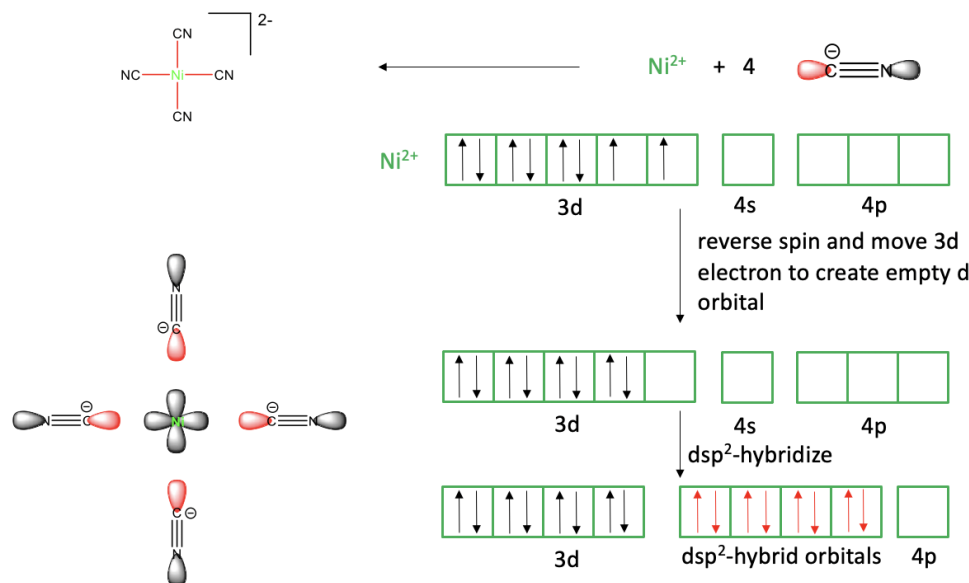


Figure 7.1.4 Valence

bond theory applied to the tetracyanonickelate (2-) square planar complex

In the valence bond picture we view the Ni-CN bonds as dative bonds, and the complex is considered an adduct of  $\text{Ni}^{2+}$  and  $\text{CN}^-$ . To explain the four bonds, the  $\text{Ni}^{2+}$  ion would need to have four empty valence orbitals. Ni is a group 10 metal and a neutral Ni atom has the electron configuration  $4s^2 3d^8$ . To create a  $\text{Ni}^{2+}$  ion we must remove the two 4s electrons, and thus the  $\text{Ni}^{2+}$  has the electron configuration  $3d^8$ . Do we have four empty orbitals available? Yes, the 4s and the three 4p orbitals are empty but again they are not equivalent and thus not suitable to explain four equivalent Ni-C bonds. Can we hybridize these orbitals? Yes, we can, but the resulting four  $sp^3$  hybridized orbitals would not be suitable to explain the square planar shape, only the tetrahedral shape. What valence bond theory suggests in this case is to reverse the spin of one of the unpaired d electrons and move it into the other half-filled d-orbital. This produces an empty d-orbital that we can now hybridize with the 4s and two of the 4p orbitals to four  $dsp^2$ -hybridized orbitals. These four orbitals have the property that their lobes point toward the vertices of a square, thus they are suitable to explain the square-planar shape. We can approach the ligands now on the bond axes to create orbital overlap between the empty  $dsp^2$  Ni and the electron lone pairs of the ligands. We can also say that the ligands donate their electron lone pairs into the hybridized metal orbitals. This produces the four covalent bonds that we need and yields a molecule of a square planar shape.

We can see that the valence bond theory can still explain the square planar shape, but only with the help of the additional assumption that one of the d-electrons gets spin-reversed and moves into another d-orbital. An assumption a theory makes should always be reasonable, so let us critique how reasonable this assumption is. Firstly, is the spin-reversal reasonable? Spin-reversal is a quantum-mechanically forbidden process, and thus it is questionable to assume that it happens. Secondly,



there is no good explanation for why the electron moves. The energy of two spin-paired electrons in the same orbital is actually higher than that of two spin-paired electrons in different orbitals. So overall, we see that valence bond theory has difficulties to explain the square planar shape. It must make assumptions that are not very plausible.

### Octahedral $d^5$ High and Low Spin Orbital Complex

The valence bond theory has also difficulties to explain so-called high spin and low spin octahedral complexes. For example, it is known from magnetic measurements for  $3d^5$  transition metal ions that they can make octahedral complexes with either one unpaired electron or five unpaired electrons, depending on the ligand. In the first case, the number of paired electrons in the d-orbitals is maximized, and we have a low-spin complex, in the other case the number of unpaired electrons is maximized, and we have a high spin complex. What approach does valence bond theory take to explain this phenomenon?

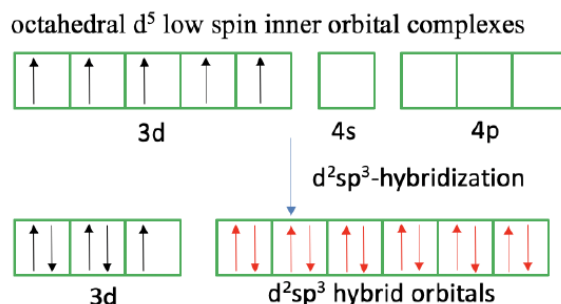


Figure 7.1.5 Valence bond theory applied to an octahedral  $d^5$  low spin-complex

In the case of a low spin-complex, valence bond theory assumes a so-called inner orbital complex. Like in the square planar complex it is assumed that unpaired electrons reverse their spins and move into other half-filled d-orbitals so that spin-pairing is maximized. In the case of a  $d^5$  ion, two electrons reverse their spin, and move into two other half-filled orbitals. This leaves one unpaired electron. We see that due to the movement of the two electrons two 3d-orbitals are empty now, and so are the 4s and the 4p orbitals. The six empty orbitals can now be combined to form  $d^2sp^3$ -hybridized orbitals that can explain the octahedral shapes. Approaching the ligands overlaps the electron lone pair at the ligand with the empty hybrid orbitals to form a dative, covalent bond. We can also say the ligands donate electron lone pairs to form six covalent bonds. We can again criticize that spin-reversal is forbidden and spin-pairing is energetically unfavorable making the approach valence bond theory takes to explain the low-spin complex unsatisfactory.

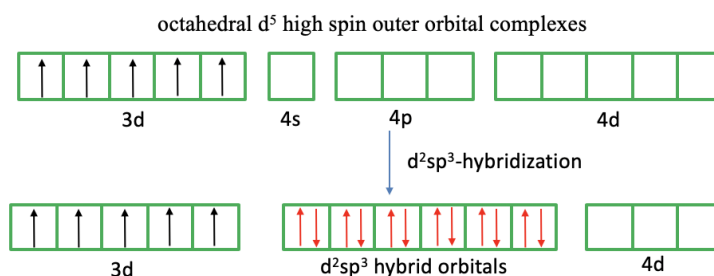


Figure 7.1.6 Valence bond theory applied to an octahedral  $d^5$  high spin-complex

What about the  $3d^5$  high spin complex (Fig. 7.1.6)? In this case we cannot pair spins to create empty d-orbitals because we need to explain five unpaired electrons. Now, valence bond theory makes another new assumption. It assumes that the outer 4d orbitals get involved in the bonding. These orbitals are empty and available for hybridization. We can therefore hybridize two 4d, the 4s, and the three 4p orbitals to form  $d^2sp^3$  hybridized orbitals. In the last step we can approach the ligands, and the ligands can donate their electron lone pairs into the transition metal d-orbitals. Now we have explained the six bonds, the octahedral shape, and the five unpaired electrons.

We can again critique the valence bond approach. What justification is there to assume that the 4d orbitals are involved. The answer is: Very little. These orbitals are just too high in energy to be considered valence orbitals. It is not reasonable to assume that they are involved in the bonding. Therefore, again, we see that valence bond theory has difficulties to explain the properties of a complex. Valence bond theory also does not explain distortions of octahedral complexes due to the Jahn-Teller effect.

### Octahedral $d^7$ High and Low Spin Orbital Complex

High-spin and low-spin complexes are not only observed for octahedral complexes of  $d^5$ -ions, but for example also for octahedral  $d^7$  ion complexes. A low-spin complex has three unpaired electrons and a high-spin complex has one unpaired electron. We will see that valence bond theory has even greater troubles to explain these compounds.

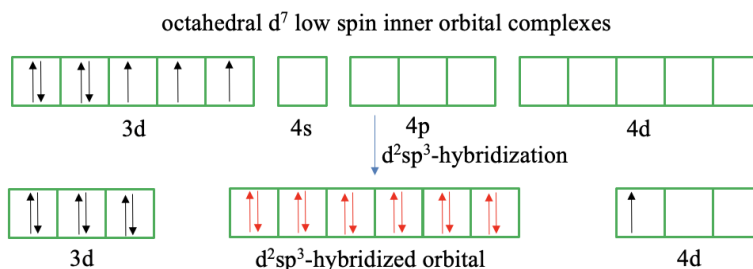


Figure 7.1.7 Valence bond theory applied to an octahedral  $d^7$  low spin-complex

In a  $d^7$  ion there are four paired and three unpaired electrons according to Hund's rule (Fig. 7.1.7). We can reverse the spin of one unpaired electron and pair it with an unpaired electron in another half-filled orbital to reduce the number of unpaired electrons to one. However, this gives us only one empty 3d orbital available for  $d^2sp^3$ -hybridization. In this case we cannot produce more empty 3d-orbitals by reversing the spin. Therefore, we must make again the questionable assumption that outer orbitals are involved in the bonding such as the 4d orbitals. Valence bond theory now suggests to move the unpaired electron from the 3d to the 4d orbital. This is simply done to create another empty 3d orbital that we need for  $d^2sp^3$ -hybridization. However, why would the 3d electron just go into another orbital of much higher energy? If we make this questionable assumption though, we have indeed six orbitals available for hybridization, and we can let the ligands donate an electron pair into the empty hybrid orbitals.

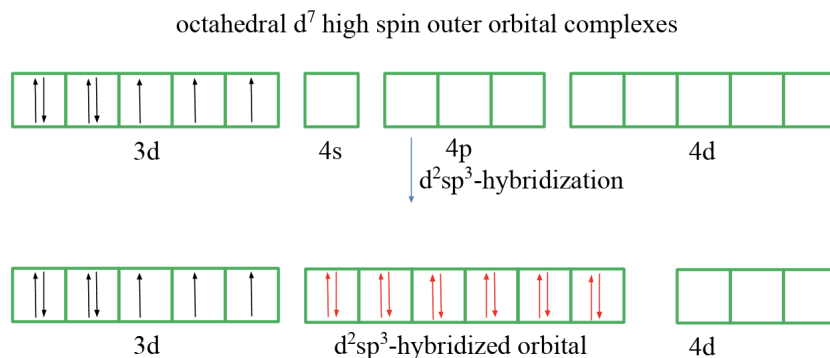


Figure 7.1.8 Valence bond theory applied to an octahedral  $d^7$  high spin-complex

Finally, let us discuss an octahedral  $d^7$  high-spin outer orbital complex (Fig. 7.1.8). In this case we cannot pair any spins in the 3d orbitals. Therefore we assume again that the 4d orbitals get involved in the bonding, and hybridize two of them with the 4s and the three 4p orbitals. The six ligands can then donate six electron pairs into the orbitals thereby creating six bonds and explaining the octahedral shape.

Overall, we see that in the valence bond theory we move around electrons as we please in order to explain shapes and magnetism of complexes without good justification. Therefore, the valence bond theory, while extremely valuable for main group compounds, is only of limited use for transition metal complexes.

### Crystal Field Theory

Now let us discuss the second bonding theory for coordination compounds, the crystal field theory. It is actually not a bonding theory because it is based on repulsive electrostatic interactions. Nonetheless, it has many features of a bonding theory in the sense that it can explain many phenomena that a bonding can explain, in particular molecular shape, magnetism, and optical properties.

What are the principles of crystal field theory? Crystal field theory assumes that the electrons in the metal d-orbitals are surrounded by an electric field which is caused by the ligand electrons. This electric field is called the crystal field. The name crystal field comes from the fact that this principle was first applied to transition metal ions surrounded by anions in crystals,