

E-Content Study Material

B. Sc. Chemistry (H)

3rd Year

Paper III B

Inorganic Chemistry

Chapter II: Metal-Ligand Bonding in Transition Metal
Complexes

Topic: Limitations of Valence Bond Theory

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Limitations of Valence Bond Theory

The valence bond theory successfully establishes a correlation between metal to ligand bonding geometry of coordination compounds. However, like any other theory, it is also not free from flaws. It has several shortcomings some of which are discussed below.

1. Although the theory gives a pictorial representation of bonding in coordination compounds, it does not have a sound theoretical basis and is essentially qualitative in nature. It does not say anything about the electronic excited states and energies associated with them. As a result, the theory fails to predict the number, positions and the intensities of the bands observed in electronic spectra of coordination compounds.

2. According to valence bond theory, the magnetic moment of a complex originates from the magnetic field generated by the spin of electrons in the metal ion. The theory gives no credence to the magnetic field generated by the orbital motion of electrons. This is a big flaw because magnetic field is generated not only by the spin motion but also by the orbital motion of electrons. The correct magnetic moment would thus be given by the combination of μ_{spin} and μ_{orbital} . This is the reason why the experimental μ value generally differs from the calculated μ_{spin} value.

3. According to valence bond theory, The complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and similar other square planar complexes of Cu(II), utilise $4dsp^2$ hybridised orbitals for bonding with the ligands. The valence bond theory suggests that the transfer of an unpaired $3d$ electrons of Cu(II) to the higher energy $4p_z$ orbital is essential to bring about $4dsp^2$ hybridisation. However, the ESR spectra reveal that the unpaired electron in such complexes is not permanently located in the $4p_z$ orbital of Cu(II). The valence bond theory also suggests that it would be easier to oxidize Cu(II) to Cu(III) in its square planar complexes since the removal of electron from the higher energy $4p_z$ orbital would be quite easy. But, it is contrary to facts. For instance, the oxidation of $[\text{Cu}(\text{NH}_3)_4]^{2+}$ to $[\text{Cu}(\text{NH}_3)_4]^{3+}$ does not occur at all.

4. The valence bond theory does not explain satisfactorily why some complexes of a metal ion in a particular oxidation state are low spin (inner orbital) while some other complexes of the same metal ion in the same oxidation state are high spin (outer orbital) complexes. For instance, while $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic, $[\text{CoF}_6]^{3-}$ is paramagnetic. According to valence bond theory, Co^{3+} in the former complex utilises the inner $(n-1)d$ orbitals for d^2sp^3 hybridisation whereas Co^{3+} in the latter complex utilises the outer nd orbitals for d^2sp^3 hybridisation. What factors compel Co^{3+} to utilise d orbitals of different principal shells in $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{CoF}_6]^{3-}$ is not explained by the valence bond theory.

5. The correlation worked out by valence bond theory between the geometry of a complex and its magnetic behavior is sometimes quite misleading. For example, according to valence bond theory, the square planar complexes of Ni(II) should be diamagnetic. This is because Ni(II) can easily make an inner $(n-1)d_{sp^2}$ hybridisation by rearranging the eight electrons in the four remaining $(n-1)d$ orbitals thereby giving rise to a square planar geometry with no unpaired electron, as shown in Fig.

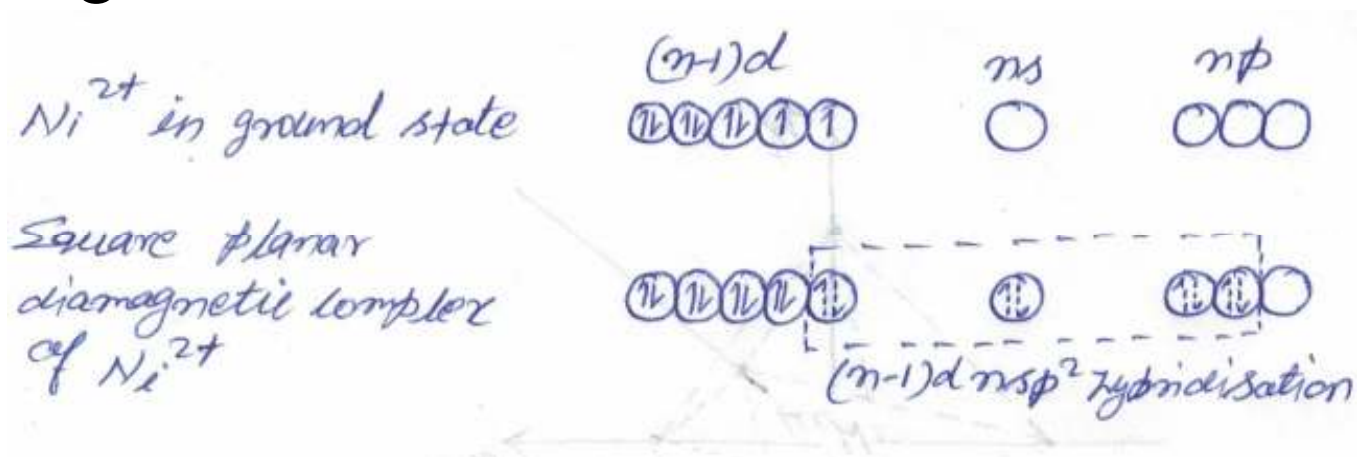


Fig. The diamagnetic square planar complex of Ni(II). The complex has no unpaired electron.

This may lead to the conclusion that all square planar complexes of Ni(II) should be diamagnetic. But actually it is not so. We come across quite a few square planar complexes of Ni(II) which are paramagnetic. Valence bond theory does make an attempt to explain this observation by postulating that in such complexes one of the unpaired $(n-1)d$ electrons of Ni^{2+} gets transferred to the vacant $4p_z$ orbital to vacate the $(n-1)d$ orbital which is required for $(n-1)d\text{ }nsp^2$ hybridisation to form a square planar complex. Such a complex would contain two unpaired electrons as shown in Fig. and would thus be paramagnetic. But it is difficult to explain why such excitation of electrons occurs in one square planar complex but not in the other.

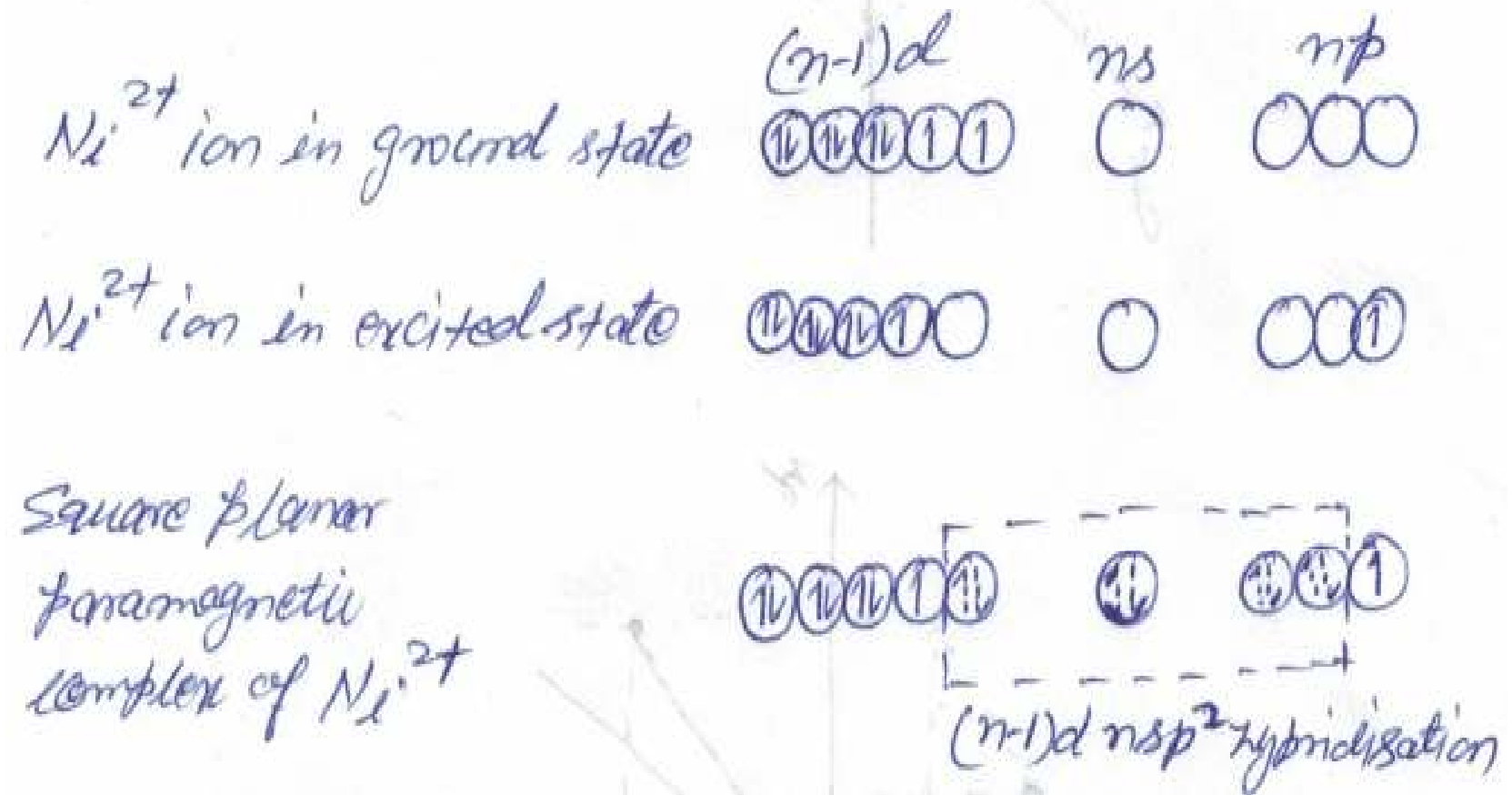


Fig. The paramagnetic square planar complex of Ni(II). The Complex has two unpaired electrons.