Comparison of Ni2+ square planar and tetrahedral complexes

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Abstract:

When Ni2+ is surrounded by a ligand field due to cyanide ligands, a square planar geometry results. However, when Ni2+ forms a complex with chloride a tetrahedral geometry results. To determine the cause of this difference, hybridization, bonding, the molecular orbital picture, and symmetry will be considered using several techniques. Because the spacings between energy levels depend on factors such as the geometry of the complex, the nature of the ligands, and the oxidation state of the central metal atom, electronic spectra of complexes can give important information about bonding and structure. EPR would be equally as useful to determine structure due to the fact that tetrahedral geometry is paramagnetic and square planar geometry is diamagnetic.

Introduction:

Square planar complexes are formed by very few metal ions, but are most commonly seen in d⁸ species. However, in square planar complexes small strong field ligands are required. Thus in Ni(Cl)₄²⁻ a tetrahedral geometry will be observed and in Ni(CN)₄²⁻ a tetrahedral geometry will be observed. This is explained by VB theory, MO theory, strong and weak field ligands, hybridization, and backbonding.

Methods:

Electronic absorption spectra bands, which are due to excitation from an occupied orbital to an empty orbital, usually are seen in the IR, visible, or UV regions. D-d transitions involve the transitions having to do with the d atomic orbitals, split by the ligand field. However these transitions are weak in complexes with a center of symmetry because they are forbidden by selection rules. However, they can be seen because of vibrational motions that break the symmetry. In a tetrahedral complex, which shows no center of inversion, the transitions are stronger but still weak compared to those involving ligand-based molecular orbitals known as charge transfer transitions. These types of transitions usually appear at higher energy and more intensely than d-d transitions.¹

Electron paramagnetic resonance (EPR) is useful in determining the magnetic properties of a complex. Due to its spin, an unpaired electron will either align itself parallel or antiparallel to an applied magnetic field. In both cases a slightly different energy results, thus making it possible to induce transitions from one level to the next. If an unpaired electron does not feel the effects of other unpaired electrons or with magnetic nuclei, a single absorption is seen. However, in many complexes the electron is at least partially delocalized over the ligands, which is shown by hyperfine splitting patterns in the EPR spectra.²

Results and discussion:

According to the valence bond theory, a complex is a Lewis acid (metal) bonded to Lewis bases (ligands) through coordinate covalent, or dative bonds. If four ligands
form a complex with a metal, either tetrahedral or square planar geometry usually result. The strength of the field felt by the metal is determined by the ligands. In the case of Ni(CN)$_4^{2-}$, Ni(II) experiences a strong field resulting in a square planar geometry. For Ni(Cl)$_4^{2-}$, Ni(II) experiences a weak field, giving a tetrahedral geometry. Both of these geometries can be described by valence bond theory.

According to valence bond theory it is possible to form square planar or tetrahedral geometry through hybridization of s, p, and d valence orbitals, which is in accordance with observed structures and magnetic properties of the complexes. Ni(CN)$_4^{2-}$ is found to be four-coordinate, square planar and diamagnetic. Because the free ion in the ground state is paramagnetic and d$^8$, the bonding picture must involve pairing of electrons and ligand-metal–ligand bond angles of 90$^\circ$. This is said to occur through hybridization of one (n-1)d, ns, and 2np orbitals that form four equivalent dsp$^2$ hybrid orbitals pointing toward each corner of a square that can form covalent $\sigma$ bonds with the ligands. The bonding electrons are provided by the ligands. However, with ligands such as Cl$^-$, Ni(II) forms four-coordinate complexes that are paramagnetic and tetrahedral. This is explained by assuming the valence d orbitals of the metal cannot accept electrons from the ligands. This would make the d orbital occupation of the complex the same as that of the free ion. Hybrid orbitals of the sp$^3$ type give $\sigma$ bonds and allow for magnetic properties. Four equivalent hybrid orbitals each containing one part s to 3 parts p are directed towards the corners of a tetrahedron. In general for a four-coordinate d$^8$ complex, diamagnetic gives square planar, and paramagnetic gives tetrahedral.$^3$

$$\text{Ni}^{2+}([\text{Ar}]3d^8) \cdot \begin{array}{c} \uparrow \downarrow \uparrow \downarrow \\ 3d \end{array} \begin{array}{c} \uparrow \downarrow \uparrow \downarrow \\ 4s \end{array} \begin{array}{c} \uparrow \downarrow \uparrow \downarrow \\ 4p \end{array}$$

$$\text{NiCl}_4^{2-} \begin{array}{c} \uparrow \downarrow \uparrow \downarrow \\ 3d \end{array}$$

$^{sp^3}$ hybrid orbitals
Electrons from Cl$^-$ ligands
Tetrahedral geometry

EPR results are experimental evidence for these magnetic properties.

For a metal in a tetrahedral ligand field, the d$_{xy}$, d$_{xz}$, and d$_{yz}$ orbitals are closer to the ligands than the d$_{x^2-y^2}$ orbitals. As a result the degeneracy of the metal d orbital is split into a set of doubly degenerate and a set of triply degenerate orbitals. In the tetrahedral character table, the d$_z^2$ and d$_{x^2-y^2}$ orbitals transform as the e representation and the d$_{xy}$, d$_{xz}$, and d$_{yz}$ transform as the t$_2$ representation. It is also evident from the tetrahedral character table that the metal s orbital has a$_1$ symmetry and the metal p orbital has t$_2$ symmetry. The linear combinations of the metal and ligand atomic orbitals of the same symmetry will show overlap along the bonding axes. It is necessary for the ligand orbitals to match the symmetries of the metal orbitals capable of bonding. If a metal orbital is capable of positive overlap with a ligand orbital along the bonding axis, a $\sigma$
bond will result. Because the $a_1$ orbital is a sphere, it is capable of bonding with all ligands. $T_2$ ligand orbitals can interact with both sets of metal $t_2$ orbitals, $p$ and $d$ orbitals, forming a $\sigma$ bond, a partially antibonding $\sigma$ molecular orbital, and an antibonding $\sigma$ molecular orbital. In a square planar geometry the four ligands lie on the $x$ and $y$ axes, thus $d_{xz}$ and $d_{yz}$ should go down in energy because the ligands are farther away than in the tetrahedral geometry. The $d_{xy}$ orbital is in the same plane as the ligands, thus increasing it’s energy, but the $d_{x^2-y^2}$ orbital is pointing directly at the ligands making it the highest in energy.
For square planar geometry, as shown above and below, the metal d orbitals are split into $e_g(d_{xz}, d_{yz})$, $a_{1g}(d_{z^2})$, $b_{2g}(d_{xy})$, and $b_{1g}(d_{x^2-y^2})$. The p level splits as well giving $a_{2u}(p_z)$ and $e_u(p_x, p_y)$. The ligand orbitals of similar symmetry, and thus capable of bonding, are $a_{1g}$, $b_{1g}$, and $e_u$. However, several metal orbitals, such as $a_{2u}$, $e_g$, and $b_{2g}$ do not match the symmetry of the ligands, resulting in nonbonding orbitals. For the low spin $d^8$ configuration, the electrons occupy the lower bonding orbitals, leaving the antibonding orbitals empty. This gives these compounds stability. It is seen that square planar geometry results in metal ions with $d^8$ electron configurations in the presence of a strong ligand field, which is true in the case of Ni(CN)$_4^{2-}$. The stronger the field, the higher in energy the $d_{x^2-y^2}$ orbital will raise, but accordingly the other orbitals lower by a corresponding amount.

Both Ni(CN)$_4^{2-}$ and Ni(Cl)$_4^{2-}$ can participate in π bonding. For Ni(Cl)$_4^{2-}$ a $p_\pi$-$d_\pi$ bond exists where donation of electron from the filled p orbitals of the Cl to empty d orbitals of the metal occur. For Ni(CN)$_4^{2-}$ a $d_\pi$-$\pi^*$ bond exists where the electron from the filled d orbitals of the metal are donated to empty π antibonding orbitals of the ligand. This results in delocalization of the electron from the metal ion towards the ligands which is known as backbonding. In Valence bond theory this is explained by π bond formation with the ligand p orbital of appropriate symmetry to the metal making it unable to π bond to N. In molecular orbital theory, backbonding is described as the metal orbital overlap with the π antibonding (CN$^-$) orbital. In either theory the electrons are shifted from the central metal towards the ligands. This makes the square planar geometry possible.
References:

1. Inorganic Chemistry, section HB
3. Ibid., p. 392.
4. Ibid., p. 392.
5. Ibid., p. 418.
6. Ibid., p. 419.
7. Ibid., p. 404.
8. Ibid., p. 394.
9. Ibid., p. 420.