Bonding theories : A Review

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Abstract

Bonding' as a crucial factor of the early post-partum entered obstetric and paediatric practice after the publication of *Maternal and Infant Bonding* in 1976 by Klaus and Kennell. The concept has held its place since, as witnessed by medical textbook accounts of it, and the perception of 'instantaneous bonding' as a vital component of the ideal birth experience has dominated media representations of childbirth and, until very recently, feminist writing. Only during the last few years has this literature taken into account research findings concerning the guilt and anxiety experienced by women whose expectations regarding 'bonding' are not realised. While it is now generally acknowledged that maternal attachment develops over an extended period of time, 'bonding' as used extensively in both popular and scientific literature conflates a wide range of meanings and blurs the boundaries between process and outcome. This facilitates the entry of ideological elements into a field which is, by its very nature, deeply significant for human experience. We therefore argue for a continuing critical appraisal of the role of 'bonding' in both general and scientific research.

Keywords: bonding**,** childbirth**,** popular discourse**,** social theory

Valence bond theory

Several theories currently are used to interpret bonding in coordination compounds. In the valence bond (VB) theory, proposed in large part by the American scientists Linus Pauling and John C. Slater, bonding is accounted for in terms of hybridized orbitals of the metal ion, which is assumed to possess a particular number of vacant orbitals available for coordinate bonding that equals its coordination number. Each ligand donates an electron pair to form a coordinate-covalent bond, which is formed by the overlap of an unoccupied orbital of the metal ion and a filled orbital of a ligand. The configuration of the complex depends on the type and number of orbitals involved in the hybridization— e.g., sp (linear), sp^3 (tetrahedral), dsp^2 (square planar), and d^2sp^3 (octahedral), in which the superscripts denote the number of orbitals of a particular type. In many cases, the number of unpaired electrons, as determined by magnetic susceptibility measurements, agrees with the theoretical prediction. The theory was modified in 1952 by the Canadian-born American Nobel chemistry laureate Henry Taube, who distinguished between inner orbital complexes (d^2sp^3) and outer orbital complexes (sp^3d^2) to account for discrepancies between octahedral complexes. The main defect of the simple VB theory lies in its failure to include the antibonding molecular orbitals produced during complex formation. Thus, it fails to offer an explanation for the striking colours of many complexes, which arise from their selective absorption of light of only certain wavelengths. From the early 1930s through the early 1950s, VB theory was used to interpret almost all coordination phenomena, for it gave simple answers to the questions of geometry and magnetic susceptibility with which chemists of that time were concerned.

Crystal field theory

Considerable success in understanding certain coordination compounds also has been achieved by treating them as examples of simple ionic or electrostatic bonding. The German theoretical physicist Walther Kossel's ionic model of 1916 was revitalized and developed by the American physicists Hans Bethe and John H. Van Vleck into the crystal field theory (CFT) of coordination, used by physicists as

early as the 1930s but not generally accepted by chemists until the 1950s. This view attributes the bonding in coordination compounds to electrostatic forces between the positively charged metal ions and negatively charged ligands—or, in the case of neutral ligands (e.g., water and ammonia), to charge separations (dipoles) that appear within the molecules. Although this approach meets with considerable success for complexes of metal ions with small electronegative ligands, such as fluoride or chloride ions or water molecules, it breaks down for ligands of low polarity (charge separation), such as carbon monoxide. It also requires modification to explain why the spectral (light-absorption) and magnetic properties of coordinated metal ions generally differ from those of the free ions and why, for a given metal ion, these properties depend on the nature of the ligands.

Ligand field and molecular orbital theories
Since 1950 it has been apparent that a more complete theory, which incorporates contributions from both ionic and covalent bonding, is necessary to give an adequate account of the properties of coordination compounds. Such a theory is the so-called ligand field theory (LFT), which has its origin in the more general, but more complicated, theory of chemical bonding called the molecular orbital (MO) theory. (Molecular orbitals describe the spatial distributions of electrons in molecules, just as atomic orbitals describe the distributions in atoms.) This theory accounts with remarkable success for most properties of coordination compounds.
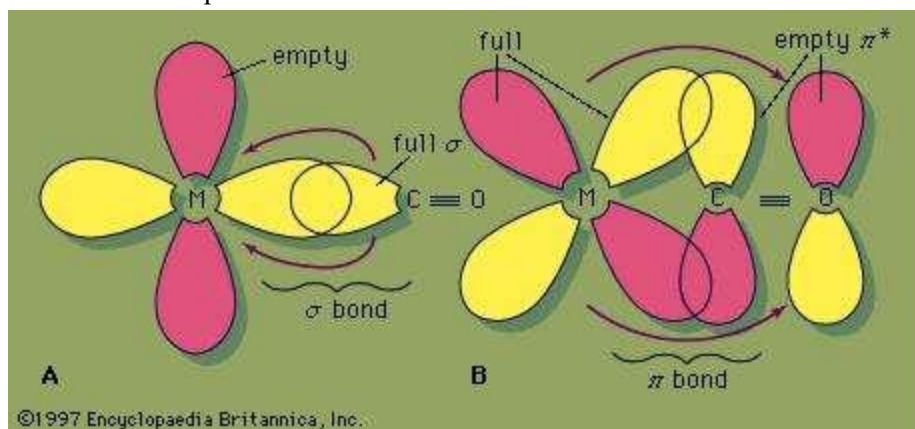
Carbon monoxide is a neutral ligand, meaning it does not carry an ionic charge. The empty π orbitals in carbon monoxide molecules accept d orbital electrons from metal atoms, thereby stabilizing the oxidation state of metal atoms. *Encyclopædia Britannica, Inc.*

The magnetic properties of a coordination compound can provide indirect evidence of the orbital energy levels used in bonding. Hund rules, which describe the order in which electrons fill atomic shells, require that the maximum number of unpaired electrons in energy levels have equal or almost equal energies. Compounds that contain no unpaired electrons are slightly repelled by a magnetic field and are said to be diamagnetic. Because unpaired electrons behave like tiny magnets, compounds that contain unpaired electrons are attracted by a magnetic field and are said to be paramagnetic. The measure of a compound's magnetism is called its magnetic moment. The complex ion hexafluoroferrate (3–) (FeF_6^{3-}) has a magnetic moment to be expected from a substance with five unpaired electrons, as does the free iron(3+) ion (Fe^{3+}), whereas the magnetic moment of the closely related hexacyanoferrate (3–) ($[Fe(CN)_6]^{3-}$), which also contains Fe^{3+}, corresponds to only one unpaired electron.
LFT is able to account for this difference in magnetic properties. For octahedral complexes the electrons of the ligands fill all six bonding molecular orbitals, whereas any electrons from the metal cation occupy

the nonbonding (*t2g*) and antibonding (*eg*) orbitals. The orbital splitting between the two sets of orbitals (*t2g* and *eg*) is designated as the orbital ligand field <u>parameter</u>, δo(where *o* stands for octahedral). Ligands whose orbitals interact strongly with the metal cation's orbitals are called strong-field ligands. For such ligands the orbital splitting is between the *t2g* and *eg* orbitals, and consequently the δo value is large. Ligands whose orbitals interact only weakly with the metal cation's orbitals are called weak-field ligands. For such ligands the orbital splitting is between the *t2g* and *eg* orbitals, and consequently the δo value is small. For transition metal ions with electron configurations d^0 through d^3 and d^8 through d^{10}, only one configuration is possible, so the net spin of the electrons in the complex is the same for both strong-field and weak-field ligands. In contrast, for transition metal ions with electron configurations d^4 through d^7 (Fe^{3+} is d^5), both high-spin and low-spin states are possible depending on the ligand involved. Strong-field ligands, such as the cyanide ion, result in low-spin complexes, whereas weak-field ligands, such as the fluoride ion, result in high-spin complexes. Therefore, in the $[Fe(CN)_6]^{3-}$ ion, all five electrons occupy the *t2g* orbitals, resulting in a magnetic moment indicating one unpaired electron; in the $[FeF_6]^{3-}$ ion, three electrons occupy the *t2g* orbitals and two electrons occupy the *eg*orbitals, resulting in a magnetic moment indicating five unpaired electrons.

An important conclusion from LFT is that two types of bonds, called sigma (σ) bonds and pi (π) bonds, occur in coordination compounds just as they do in ordinary covalent (organic) compounds. The more usual of the two are σ bonds, which are symmetrical about the axis of the bond; π bonds, which are less common, are unsymmetrical with regard to the bond axis. In coordination compounds, π bonding may result from donation of electrons from ligands, such as fluorine or oxygen atoms, to empty *d* orbitals of the metal atoms. An example of this type of bonding occurs in the chromate ion, $(CrO_4)^{2-}$, in which the oxygen atoms donate electrons to the central chromium ion (Cr^{6+}). Alternatively, electrons from *d* orbitals of the metal atom may be donated to empty orbitals of the ligand. This is the case in the compound tetracarbonylnickel, $Ni(CO)_4$, in which empty π orbitals in the carbon monoxide molecules accept *d*-orbital electrons from the nickel atom.
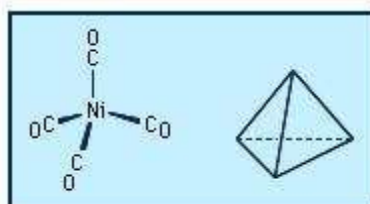
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Empty π orbitals in carbon monoxide molecules accept *d* orbital electrons from nickel to form the compound tetracarbonylnickel, $Ni(CO)_4$.*Encyclopædia Britannica, Inc.*

Ligands may be classified according to their donor and acceptor abilities. Some ligands that possess no orbitals with symmetry appropriate for π bonding, such as ammonia, are σ donors only. On the other hand, ligands with occupied *p* orbitals are potential π donors and may donate these electrons along with the σ-bonding electrons. For ligands with vacant π^* or *d* orbitals, there is a possibility of π back bonding, and the ligands may be π acceptors. Ligands can be arranged in a so-called spectrochemical series in order from strong π acceptors (correlated with low spin, strong field, and large δ values) to strong π donors (correlated with high spin, weak field, and small δ values) as follows: CO, CN^- > 1,10-phenanthroline > NO^{2-} > en > NH_3 > NCS^- > H_2O > F^- > $RCOO^-$ (where R is an alkyl group) > OH^- > Cl^- > Br^- > I^-. Additional ligands could be added here, but such an expanded list would not be very useful, because the order of the ligands is affected by the nature and charge on the metal ion, the presence of other ligands, and other factors.

The energy of the light absorbed as electrons are raised to higher levels is the difference in energy between the *d* orbital levels of transitional metal complexes. As a result, electronic spectra can provide direct evidence of orbital energy levels and information about bonding and electronic configurations in complexes. In some cases, these spectra can also provide information about the magnitude of the effect of ligands on the *d* orbitals of the metal (δ_o). The energy levels of *d*-electron configurations, as opposed to the energies of individual electrons, are complicated, since electrons in atomic orbitals can interact with each other. Tetrahedral complexes give more intense absorption spectra than do octahedral complexes. For *f*-orbital systems (lanthanoids, 4*f*n, and actinoids, 5*f*n) the LFT treatment is similar to that for *d*-orbital systems. However, the number of parameters is greater, and, even in complexes with cubic symmetry, two parameters are needed to describe the splittings of the *f* orbitals. Furthermore, *f*-orbital wave functions are not well known, and interpretation of the properties of *f*-electron systems is much more difficult than it is for *d* systems. In an effort to overcome such difficulties with *f*-orbital systems, an approach called the angular overlap model (AOM) was developed, but it proved of relatively little value for these systems.

Conclusion

The current study provides experimental insight into the chemical bonding in 1,3,4-trinitro-7,8-diazapentalene. In particular, conjugation in the five-membered rings is established from the topological analysis of the electron density. Asymmetry in the electrostatic potential owing to the proximity of the two nitro groups on one side of the molecule is also demonstrated. The nature of the OH, OO, ON and OC intermolecular interactions has been characterized.

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