transition metal complexes according to the scheme:

$$S + ne + nH^+ \xrightleftharpoons{Cat} SH_n$$

These processes as well as the oxidation, *i.e.*

$$2H_2O - 4e - 4H^+ \xrightarrow{Cat} O_2,$$

may proceed in coordination sphere of a polynuclear metal complex as multi-electronic reactions.

Thus N_2 can be reduced to N_2H_4 (without free N_2H_2 as an intermediate) and directly to NH_3. CO is reduced to CH_3OH (without intermediate formation of CH_2O). H_2O can be oxidized to O_2 (without H_2O_2 as an intermediate).

The mechanism can be regulated by changing of flow of electrons, pH of the solution or composition of a solvent, *e.g.* four-electron reduction of N_2 to N_2H_4 can be replaced by six-electron reduction of N_2 to NH_3.

Use of Electron Spin Resonance Spectroscopy to Study the Interaction between Cobalt Schiff Base Complexes and Phosphines or Phosphites in Solution

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E.s.r. measurements on frozen solutions of a wide range of phosphine or phosphite adducts of Co(II) Schiff base complexes have given well resolved spectra exhibiting cobalt and phosphorus hyperfine structure. From analysis of the ^{31}P hyperfine tensor, the R–P–R bond angle can be deduced in the phosphine or phosphite, PR_3. The calculated spin densities in the cobalt and phosphorus orbitals allows a determination of the relative contributions of σ- and π-bonding in the Co–P bond and their influence upon the phosphine or phosphite bond angle. From a full analysis of the ^{31}P polarisation tensor, a correlation is found between its magnitude and the magnitude of the splitting of the cobalt d_{xz} and d_{yz} orbitals. In analysing the ^{59}Co spin Hamiltonian parameters, used is made of the theory of McGarvey and the approximations of Attanasio.

References

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Nuclear (^1H, ^{13}C) Magnetic Resonance Studies of the Proton Transfer Processes in Hydrogen Bonded Complexes in Aprotic Solvents

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Nuclear (^1H, ^{13}C) magnetic resonance methods have been widely applied to the study of electronic structure of the hydrogen bond, proton transfer phenomena and dynamics of hydrogen bond formation in the phenol–triethylamine complexes in the temperature range of 100–300 K. Phenolic acids with triethylamine form a 1:1 complex whose nature in solution may be a simple hydrogen-bonded molecular complex or a hydrogen-bonded ion-pair depending on the acidic property of phenol.

Thermodynamic and kinetics quantities of this molecular complex/ion pair tautomerism have been evaluated and results obtained will be discussed in relation to the potential energy profile of the hydrogen bonds. In addition the chemical shift of proton directly engaged in the hydrogen bond and the chemical shift of the oxygen bearing carbon of the phenol ring in a molecular complex ($O–H\cdots N$) and in ion-pair ($O^-\cdots H–N^+$) have been estimated. Those NMR parameters will be discussed in relation to the electronic structure of the hydrogen bond.

Some Applications of Liquid Crystals in Organic Chemistry

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Some applications of thermotropic liquid crystals (LC) such as anisotropic solvents for stereochemical, spectrochemical and reactivity studies are presented.

The study of cholesteric mesophases induced in a nematic LC by traces of optically active substances having a single asymmetric centre gives information about the configuration and/or the relative size of the groups connected to the chiral carbon or sulphur atom.

Liquid crystalline solvents, transparent in the UV–Visible region, can be used as orientating matrices