

nia molecules combined. The tetraamminecopper(II) complex has four ammonia molecules at the equatorial position and two water molecules at the axial one. The Cu–NH<sub>3</sub> bond distance within the complex is longer by 0.1 Å than the Cu–OH<sub>2</sub> distance within the aqua complex. On the contrary, the axial Cu–OH<sub>2</sub> bond within the tetraamminecopper(II) complex shortens by *ca.* 0.1 Å. In a higher copper(II)–ammine complex formed by the addition of a large excess of ammonia to the solution (although the composition of the complex is not determinable either Cu(NH<sub>3</sub>)<sub>5</sub>(OH<sub>2</sub>)<sup>2+</sup> or Cu(NH<sub>3</sub>)<sub>6</sub><sup>2+</sup> by the present method), the length of the Cu–NH<sub>3</sub> bond at the equatorial position within the complex shortens to 1.94 Å, whereas the length of the Cu–NH<sub>3</sub> bond at the axial position is remained practically unchanged by replacement of the water molecule(s) within the tetraamminecopper(II) complex with ammonia. Such complicated changes in the bond lengths within the copper ammine complexes are not explained by simple theories of coordination chemistry.

The diamminesilver(I) complex has a linear structure, which is similar to the structure of the aqua silver(I) complex. However, the bond length between the silver atom and the ammonia molecules within the diammine complex is much shorter than the corresponding metal–ligand distance within the aqua complex. Free solvent molecules are not found in the region less than 3 Å from the central silver atom of the both complexes.

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### Classical Ionic Fluids in the Mean Spherical Approximation

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The analytical solution of the mean spherical approximation (MSA) has been used to calculate excess thermodynamic properties of aqueous and non-aqueous solutions of 1–1, 1–2, 1–3, 1–*n* electrolytes. For some solutions and a few molten salts also structure functions and pair correlation func-

tions have been obtained. The possibility of use of MSA to simulate systems of primary interest in the framework of enhanced oil recovery is also discussed. Finally, MSA pair correlation functions are compared with the Debye–Hückel correlation functions in an attempt to compute higher order graph contributions beyond the ring diagrams which yield the D–H approximation.

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### Polymer Attached Catalysts

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Homogeneously catalyzed reactions usually take place at low temperatures and pressures and with high selectivity. Heterogeneous catalysts however have many engineering advantages.

A practical limitation to performing homogeneously catalyzed reactions in liquid phase is the difficulty of separating the product from the catalysts. To overcome this difficulty homogeneous catalysts have been attached to a variety of insoluble supports, with the aim of acquiring the properties of insolubility while maintaining the reactivity exhibited in solution.

The liquid phase, however, plays an important role in polymer supported catalysts and the solvent–substrate–support interactions have a large influence on the catalytic activity and selectivity of this type of catalysts. This property associated with the high dependence of the reduction rate on size and rigidity of the substrate suggests that reduction takes place within the resin, where the active sites are located, rather than at its surface, and that the catalyst could ‘remember’ conditions used during the synthesis.

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### Catalytic Red–Ox Reactions of Small Molecules with Participation of Solvent Protons

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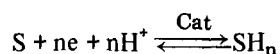
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Small molecules such as C<sub>2</sub>H<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub> *etc.* can be reduced in protic media in the presence of

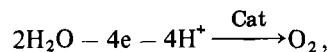
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transition metal complexes according to the scheme:



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



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  $NH_3$ .

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### 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  $\sigma$ - and  $\pi$ -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

B. R. McGarvey, *Canad. J. Chem.*, 53, 2498 (1975); D. Attanasio, G. Dessy, V. Fares and G. Pennesi, to be published.

### 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.

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### 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