present as a neat solvent will be discussed. The emphasis will be done to the changes in the structure of the complexes as a result of the above interactions. Furthermore, the main conclusions will be transferred to some reaction systems in which the copper(II) chelate complexes are used as catalysts. These studies seem to be of great importance for understanding the pathways of some chemical and biochemical reactions and specially the way in which the 'neutral' copper(II) chelate complexes are transformed into catalytically active forms through the interactions mentioned above.

An NMR Study of Solvent Interactions in a Paramagnetic System

R. M. GOLDING

The University of New South Wales, P.O. Box 1, Kensington, N.S.W. 2033, Australia

The temperature dependence of the proton nmr spectra of dithiocarbamato iron(III) complexes is markedly solvent dependent. A study is made of the temperature dependence of the nmr shifts for the N–CH_2 protons in tris(N, N-dibutyldithiocarbamato)-iron(III) in acetone, benzene, carbon disulphide, chloroform, dimethylformamide, pyridine and some mixed solvents. This contribution shall outline first how the nmr shifts may be interpreted in terms of the Fermi contact interaction and the dipolar term in the multipole expansion of the interaction of the electron orbital angular momentum and the electron spin dipolar–nuclear spin angular momentum. This analysis yields a direct measure of the effect of the solvent system on the environment of the transition metal ion. The results are analysed in terms of the crystal field environment of the transition metal ion with contributions from (*a*) the dithiocarbamate ligand (*b*) the solvent molecules and (*c*) the interaction of the effective dipole moment of the polar solvent molecule with the transition metal ion complex. The model yields not only an explanation for the unusual nmr results but gives an insight into the solvent–solute interactions in such systems.

Study of Cobalt Complexes – Models of some Natural Systems

B. JEZOWSKA-TRZEBIATOWSKA

Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Poland

We have discovered and investigated the systems capable of activation and transportation in solution the small gas molecules: O_2, NO and CO_2, modelling not only the natural O_2 and CO_2 carriers, but also some enzymatic systems. These are: *1*) Co(II) complexes with imidazole and amino-acids, carriers of the molecular oxygen and NO in aqueous solutions over the pH range 7–9; *2*) Co(II) complexes with bidentate Schiff bases, O_2 and CO_2 carriers in non-aqueous solutions; *3*) Co(II) complexes with monoamines, active in non-aqueous solutions as oxygen carriers. We have examined the structure of several forms of those complexes (with and without the coordinated gas molecule), the equilibria between them in solutions and their contribution to the other equilibria. We have determined the influence of ligands and of a solvent on the equilibria and on the effectiveness of the gas transportation. Moreover, we have examined the catalytic oxidation reaction of hydrazine and its derivatives with O_2 in the system: Co(II)–bidentate Schiff basis–hydrazine–O_2, modelling some desaminases.