donors show additional splittings $\Delta\delta$ in the presence of *optically active* acceptors (Fig. 1, bottom) which are absent (Fig. 1, top), if *racemic* acceptors are applied [2]. Similarly, the signals of racemic acceptors are split in the presence of optically active donors. In some cases, assignments of individual lines to specific diastereomeric complexes have been achieved by using a *nonracemic* mixture of one component and a pure enantiomer of the other component [3].

The comparison of ^{1}H NMR shifts $\bar{\delta}$ for the mixtures with those of the pure components [4] as well as the temperature dependence [2] of $\bar{\delta}$ for the mixture provide further evidence of association. These relative shifts are caused predominantly by the diamagnetic anisotropy of the partner in the complex. They enabled us to propose a model for the *orientation* (Fig. 2) of the components for some of the complexations studied. The magnitudes of the above splittings $\Delta\delta$ (*e.g.* Fig. 1) give some support to this proposal.

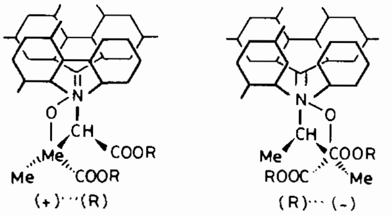

Fig. 2. Average diastereomeric 1:1 complexes between (R)-2-(N-carbazolyl)-propionic esters and (±)-2-(2,4,5,7-tetranitro-9-fluorenylideneaminoxy)-propionic esters.

Results [5] with chiral or prochiral cations and optically active anions will be mentioned. In this case, similar ^{1}H NMR effects are brought about by *cation–anion attraction.* Possible applications for the measurement of enantiomeric purity [6] will be discussed.

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^{31}P and ^{1}H NMR Characterization of Stereoisomeric Macrocyclic Nickel(II) Complexes with a Tetraphosphane Ligand

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Several studies on metal complexes formed by macrocyclic ligands have shown that these compounds provide stimulating examples for studying the conformational properties of the molecules. Recent synthetic developments in this laboratory have provided some ideal ligands for investigating the configurational properties of polyphosphane macrocyclic complexes. As an example, the results of ^{31}P and ^{1}H NMR investigations on some stereoisomeric nickel(II) derivatives of the 4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclooctadecane {|18|aneP_4O_2} are here reported.

The |18|aneP_4O_2 ligand can exist in five basic structural forms (Fig. 1), as determined by the distribution of phosphorus atom configurations with respect to the aliphatic chains spanning the phosphorus atoms themselves. Three of these forms [(a), (b), and (c)] are nonenantiomeric, whereas (d) and (e) forms exist together their respective enantiomers. The five forms are interconvertible diastereoisomers; however, because of their high temperature of

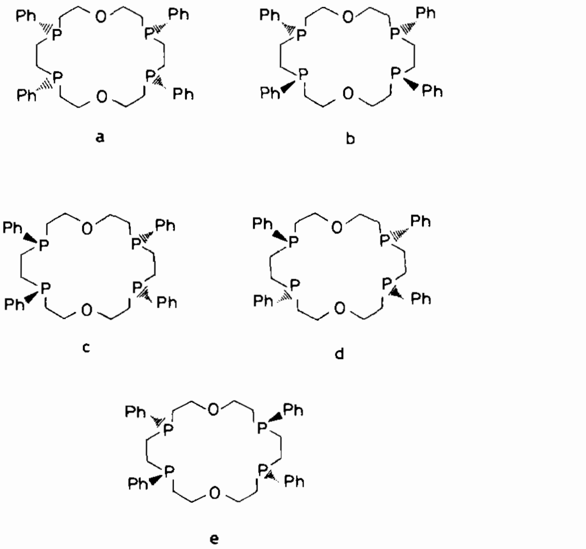

Fig. 1. The five possible diastereoisomers of |18|aneP_4O_2 ligand.

racemization, they can, in principle, be isolated as free ligands at room temperature.

Two isomeric forms I and II of the |18|aneP_4O_2 ligand have been isolated and their nickel(II) tetrafluoborate derivatives have been synthesized and characterized. Conductometric, magnetic and spectroscopic measurements indicate that the latter compounds contain square planar $\{Ni(|18|aneP_4O_2)\}^{2+}$ cations, the nickel(II) ion being coordinated to the four phosphorus atoms. The ^{31}P NMR spectrum of isomer I is reported in Fig. 2 and shows a pattern of resonances which indicates the presence of four nonequivalent phosphorus atoms. The (d) configuration, therefore, is proposed for this stereoisomer. Both ^{1}H and ^{31}P NMR spectra indicate a symmetric configuration for isomer II. Since from ^{1}H NMR trace it appears that the ethylenic chains spanning the phosphorus atoms adopt the *gauche* conformation, only configurations (b) and (e) can be proposed for this stereoisomer. Preliminary X-ray diffractometric data indicate that the configuration (b) is to be assigned to the isomer II. Attempts to isolate and characterize all the possible isomers are actually in progress.

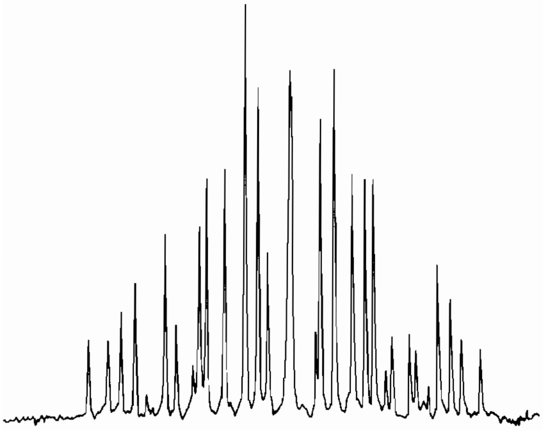

Fig. 2. ^{31}P NMR spectrum at 30 °C of d_6-DMSO solution of $\{Ni(|18|aneP_4O_2\text{-}I)\}^{2+}$.

NMR Studies on Ion Pairing in Solution

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A series of compounds of general formula (ZR_4)-$(MPPh_3X_3)$ Z = N, P; R = butyl, propyl, ethyl; M = Co, Ni, Zn; X = Br, I, has been prepared, and their chloroform or dichloromethane solutions have been investigated by means of T_1, T_2, and chemical shift measurements on ^{1}H, ^{13}C, and ^{31}P nuclei. Earlier proton NMR data on a limited number of the above compounds were interpreted on the ground of purely dipolar interactions between the cations and the paramagnetic complexes [1, 2], although later reports on ^{14}N and ^{31}P shifts [3, 4] suggested the existence of some contact contributions. The thorough investigation of the above systems allows to generalize their NMR behavior as follows:

1) all of the R protons undergo upfield shifts in the cobalt(II) and downfield shifts in the nickel(II) compounds, with respect to the zinc analogues; their absolute values decrease with increasing distance from the Z hetero atom along the alkyl chain;

2) all of the R carbons experience downfield isotropic shifts in both cobalt(II) and nickel(II) compounds, again decreasing in magnitude from C_1 to C_n;

3) the ^{31}P nucleus of the cation, analogously to the nitrogen atom in the corresponding compounds [3], always experiences downfield shifts like the attached carbon atoms;

4) the longitudinal and transverse relaxation enhancements (T_1^{-1} and T_2^{-1}), measured with respect to the zinc analogues, are generally small but are only slightly attenuated passing from the central atom to the outer atoms of the cation, even taking into account the difference in gyromagnetic ratios. The T_2^{-1} values are always larger than the T_1^{-1} values of the same nucleus.

Systems of the type $(C_4H_9)_4Z_2(MX_4)$ and $(C_4H_9)_4Z(MquinX_3)$ have also been considered for comparison purposes. The data on these systems are in agreement with the above results, showing that they do not depend on any particular geometry of the paramagnetic anion considered.

While the absolute magnitude of the observed paramagnetic effects is rather small, thus confirming that only weak interactions are operative, a qualitative analysis shows that even in such weakly coupled systems the true "through space' dipolar coupling is very small; most of the measured effect is due to some unpaired spin delocalization, since the ratios between proton and carbon isotropic shifts are different in sign in cobalt and nickel compounds. The occurrence of such spin delocalization is confirmed by the difference in T_1 and T_2 values. Since the R_4Z^+ cations experience relevant contact contributions, point-dipole equations for shifts and relaxation times [5–7] cannot be used to perform structural analysis. Furthermore, ^{1}H and ^{13}C measurements at decreasing sample concentrations show that, besides the expected general decrease of the paramagnetic effects due to progressive uncoupling of the ions, there is also a sizeable change in the isotropic shift *ratios* suggesting the existence of more than one geometric arrangement of the ionic couples.