promote ion pairing with the dianionic COT moiety of the trianion thus slowing the intramolecular electron transfer process. These parameters are currently under study.

The anion radical of (II) at 10 °C in HMPA–THF solution again indicates that the unpaired electron resides exclusively in one of the COT moieties. Esr spectral data clearly indicates that –Si(CH₃)COT acts as an electron withdrawing group. This is probably the reason why the electron does not exchange between the COT's, since the unpaired electron resides primarily in a COT molecular orbital which has a node in the substituted position. Interestingly, an esr signal for COT⁻ is observed simultaneously with that of the compound. This signal grows as a function of time, suggesting that there is slow decomposition of one of the C–Si bonds. Experiments are underway to generate the trianion radical of (II) at low temperatures to see if electron transfer can be detected. Ion pairing perturbations will be also investigated.

Compound (III) has been recently synthesized. Electron transfer between COT moieties in (III⁻) is definitely expected. The transfer rate will be investigated as a function of both temperature and ion pairing parameters.

Electron Spin Relaxation in the Study of Boundary Layers at the Liquid–Solid Interphase

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The electron spin relaxation of transition metal ions is largely sensitive towards structural changes of the complex and towards mobility alterations of the solvent. In the case of Cu(II) (S = 1/2), structural changes influence both the magnetic parameters (g and A tensors) and the line width as a consequence of the relaxation mechanisms dominating in solution (spin-rotation and A and g anisotropies modulation). Solvent mobility variations also alter the line width, at low and high temperature, in opposite ways. In the case of Mn(II) (S = 5/2), structural changes influence the zero-field splitting term, thus effecting the line width, without appreciably modifying the line position (static term in the spin Hamiltonian). Decreased solvent mobility increases the correlation time for the motion and therefore the line width (dynamic term in the spin Hamiltonian).

The liquid mobility at the solid–liquid interface is expected to be decreased and to induce large effect on the line width of paramagnetic probes in the boundary layers. From a line width analysis, the cor-

relation times for the motion can be calculated as a function of the distance from the surface.

The above procedure is applied to liquid–solid interphases in which SiO_2, Al_2O_3, TiO_2, and carbon were the porous solid supports, and water, NaOH water solution, and organic fluids were the liquids. The probes used were $Mn(H_2O)_6^{2+}$, $Cu(H_2O)_2^{2+}$, $Cu(OH)_4^{2-}$, and $Cu(acac)_2$.

Diastereomeric Electron-Donor–Acceptor Complexes

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An electron–donor acceptor (EDA) interaction has been assumed to contribute, besides hydrogen bonding, to the formation of certain diastereomeric complexes [1]. We have now shown, for different molecular systems, the existence of diastereomeric complexes which seem to be held together by EDTA attraction *exclusively*.

Among others, carbazole derivatives were chosen as π-donors and fluorenone derivatives as π-acceptors [2] (*e.g.* Fig. 1). The ¹H NMR signals of racemic
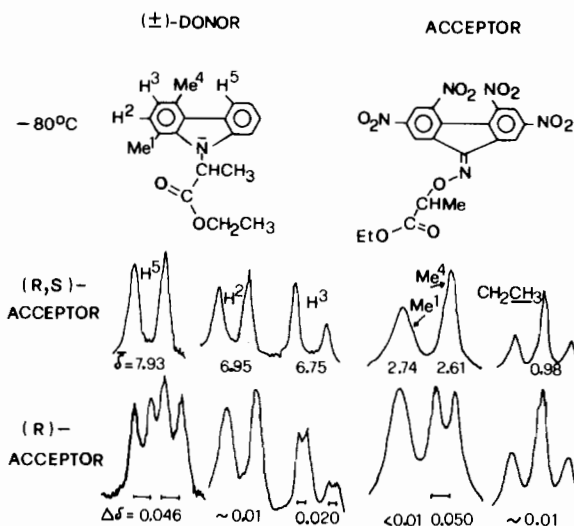

Fig. 1. ¹H NMR in [D₆]acetone of a racemic donor in the presence of 1.10 equivalents of (R, S)- or (R)-acceptor, respectively. Δδ: Shift difference between protons of (+)- and (−)-donor, determined from splittings or estimated from linewidths.