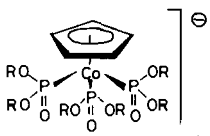
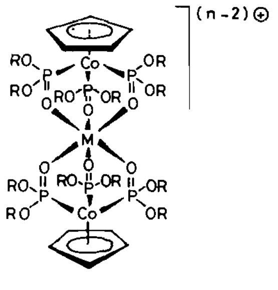


(1)



(2) M^{n+} = Co^{2+}
(3) Hg^{2+}
(4) Ca^{2+}
(5) Sn^{2+}
(6) Cu^{2+}
(7) Eu^{3+}
(8) In^{3+}
(9) Co^{3+}

The spin crossover has also been studied in solution to assess the influence of the solvent on the thermodynamic parameters of the singlet–quintet equilibrium. It has been found that the ΔH and ΔS values for the spin transition are nearly independent of the nature of the solvent [7]. The equilibrium is however markedly influenced by the substituents R = CH_3, C_2H_5, $^{i}C_3H_7$, on the ligands (1).

References

1 W. Kläui, *Z. Naturforsch., 34b,* 1403 (1979).
2 W. Kläui and K. Dehnicke, *Chem. Ber., 111,* 451 (1978).
3 E. Dubler, L. Linowsky and W. Kläui, *Transition Met. Chem., 4,* 191 (1979).
4 W. Kläui, *J. Organometal. Chem.,* in print.
5 N. El Murr, A. Chaloyard and W. Kläui, *Inorg. Chem., 18,* 2629 (1979), and unpublished results.
6 W. Kläui, *J. Chem. Soc. Chem. Commun., 1979,* 700.
7 P. Gütlich, B. R. McGarvey and W. Kläui, *Inorg. Chem.,* submitted for publication.

MCD Studies of Lanthanide Ions in Aqueous Solution

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Magnetic circular dichroism signals result from the interplay of different factors. These are external factors as the magnitude of the magnetic field, optical pathway and temperature as well as intrinsic molecular factors as spectral bandwidth, transition probabilities and magnetic moments. Therefore the MCD technique offers interesting possibilities both from an analytical and a fundamental point of view.

It will be shown that symmetry conclusions about the surrounding of lanthanide ions in solution can be derived from an analysis of the *sign* and magnitude of the MCD signals. This will be illustrated for Eu^{3+} and Pr^{3+} in different solvents: water, ethanol and acetonitrile.

Figure 1 gives the spectra of the perchlorates in aqueous solution (see page X24).

Electronic Rearrangements Induced by Weak Intermolecular Forces: Orbitally Degenerate Sandwich Complexes

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The vast majority of all molecules have an orbitally non-degenerate ground state characterized by an electronic wavefunction ψ_{el} depending only weakly on the nuclear coordinates R. In contrast, for orbitally degenerate or near-degenerate molecules quite drastic electronic rearrangements can be induced by relatively weak intermolecular forces provided by nonpolar solvents or molecular solid host lattices. In paramagnetic systems changes in the electronic wavefunction can most conveniently be detected and analyzed by using EPR spectroscopy.

Paramagnetic sandwich complexes of the metallocene series $M(cp)_2$ exhibit two types of orbital degeneracies: Jahn–Teller degeneracies (d^7 systems as $Co(cp)_2$ and $Ni(cp)_2^+$, low-spin (d^5 systems as $Mn(cp)_2$ and $Fe(cp)_2^+$) and low-spin/high-spin equilibria (d^5 systems as $Mn(cp)_2$). By diluting these complexes and ring-substituted derivatives in a large variety of diamagnetic host systems we have been able to control the $^6A/^2E$ equilibrium of $Mn(cp)_2$ by influencing the metal-to-ring distance and by changing the degree of ring-alkylation; similarly we have been able to vary the relative weights of the two electronic states contributing to the twofold degenerate electronic ground state of d^5 and d^7 systems to a large degree by variation of the local asymmetric fields offered by the lattice sites of the host systems.

In the free gaseous state for all orbitally degenerate d^5 and d^7 metallocenes the Jahn–Teller distortions in the C_5H_5 rings remain entirely dynamic, *i.e.*