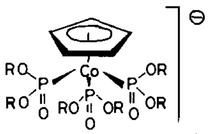
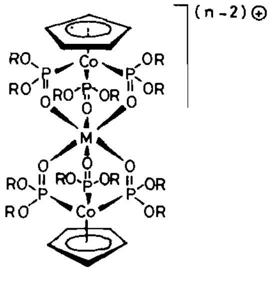


(1)



(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, $^iC_3H_7$, 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 Chem., 18,* 2629 (1979), and unpublished results.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

C. GÖRLLER-WALRAND

Katholieke Universiteit Leuven, Laboratorium voor Analytische en Anorganische Scheikunde, Celestijnenlaan 200 F, 3030 Heverlee, Belgium

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

L. ZOLLER and J. H. AMMETER

Institute of Inorganic Chemistry, University of Zurich, Winterthurerstrasse 190, 8057 Zurich, Switzerland

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.*

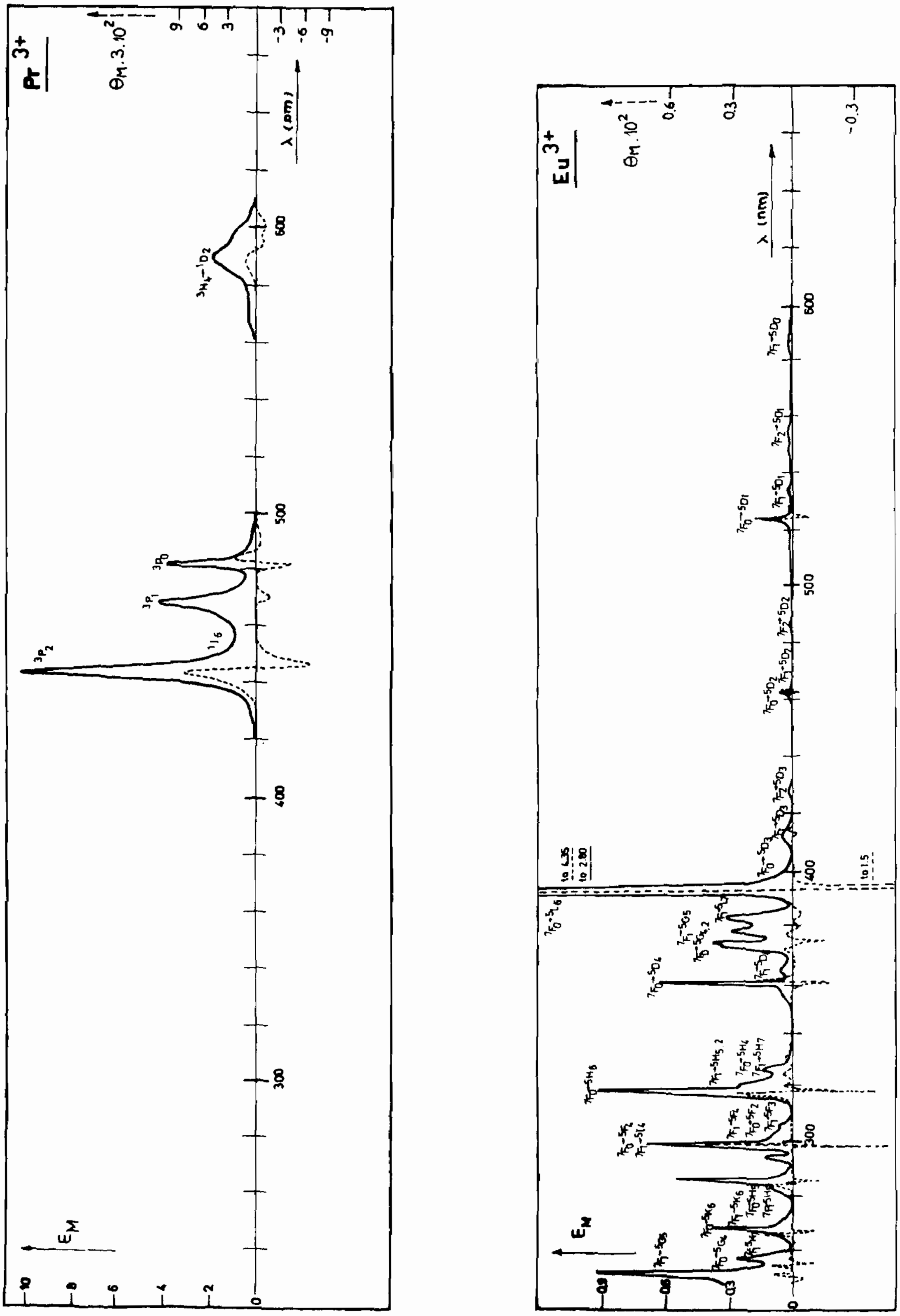


Fig. 1. Spectra of Eu^{3+} and Pr^{3+} *in aqueous solution–absorption . . . .* MCD.

the Jahn–Teller stabilization energy E_{JT} never exceeds the energy of a quantum $h\nu$ of the corresponding active vibrational modes substantially. The degree of covalent delocalization of the singly occupied degenerate metal 3d orbital over the ligand rings correlates well with Jahn–Teller distortion increasing strongly along the series $\mathrm{Fe(cp)_2^+} < \mathrm{Mn(cp)_2} < \mathrm{Co(cp)_2} < \mathrm{Ni(cp)_2^+}$.

This finding agrees with the predictions of semiempirical MO calculations. In the solid state, by systematic variation of the host lattice we were able to observe a stepwise transition from a purely dynamic Jahn–Teller effect to the static distortion limit in the case of cobaltocene. Alkyl substituents at the rings influenced the cobaltocene EPR spectra in the same way as asymmetric lattice potentials.

Electrical Anharmonicity for the OH Stretching Vibration of Methanol and its Hydrogen Bonded Complexes

SURJIT SINGH, DAG SCHIÖBERG and WERNER. A. P. LUCK

Fachbereich Physikalische Chemie der Philipps-Universität Marburg, Auf den Lahnbergen, D-3550 Marburg/Lahn, F.R.G.

We have calculated the first and second dipole moment derivatives for a number of hydrogen bonded systems involving methanol and a variety of organic bases. Herman and Shuler's [1] expressions for the intensities of fundamental and first overtone are employed for the calculations. Both ++ and +– combinations of experimental values of transition moment integrals R_0^1 and R_0^2 are considered. Given below are the typical values of μ_1 and μ_2 for the two sign combinations in the case of dilute solutions of CH_3OH in CCl_4 representing free OH and CD_3OH in DMSO-d_6 as well as self associated CD_3OH in CD_3OD. It is found that for all the systems considered both for ++ and +– combinations μ_1 as well as μ_2 increase on hydrogen bonding. Often a reference is made in the literature that the intensity of the first overtone band of XH stretching vibration decreases on hydrogen bonding whereas that of the fundamental increases. On the basis of these observations a decrease in the overtone intensity can be explained on the basis of the fact that the negative contribution to the overtone intensity from an increase in the first derivative of the dipole moment supersedes the positive contribution from the increase in the second derivative of the dipole moment. This explanation is quite justified as it can be noticed from the above values that whereas μ_1 increases about 4 to 5 times on hydrogen bonding in the cases considered in these studies, μ_2 only increases by 50 to 10%.

Methanol in	++ comb.		+– comb.	
	$\mu_1 \times 10^{20}$	$\mu_2 \times 10^{20}$	$\mu_1 \times 10^{20}$	$\mu_2 \times 10^{21}$
CCl_4	4.567	1.017	4.770	8.094
DMSO-d_6	20.443	1.641	20.750	3.943
CD_3OD	23.545	2.033	23.952	4.936

This observation is similar to the prediction made by Di Paolo, Bourderon and Sandorfy [2] on the basis of their theoretical model calculations on the influence of Electrical Anharmonicity on infrared intensities in hydrogen bonded systems. However, contrary to their predictions it is rather clear from these studies that the decreasing intensities of first overtones on hydrogen bonding can be explained by taking +– combinations as nicely as from ++ combinations of transition moment values.

References

1 R. C. Herman and K. E. Schuler, *J. Chem. Phys., 22,* 481 (1954).

2 T. DiPaolo, C. Bourderon and C. Sandorfy, *Can. J. Chem., 50,* 3161 (1972).

Synthetic Models for Cytochrome-C Oxidase: Magnetic and Mössbauer Effect Studies of Binuclear Fe(III) Porphyrin–Cu(II) Complexes

K. S. MURRAY*, K. J. BERRY

Department of Chemistry, Monash University, Clayton, Vic. 3168, Australia

P. E. CLARK

Department of Physics, Monash University, Clayton, Vic. 3168, Australia

M. J. GUNTER, L. N. MANDER and G. M. McLAUGHLIN

Research School of Chemistry, Australian National University, Canberra, A.C.T. 2600, Australia

Recent e.s.r., magnetic susceptibility and m.c.d. measurements have indicated the presence of a