have investigated the properties of several discrete mixed valence complexes with different numbers of metallic sites, in order to propose them as models for the corresponding nonstoichiometric metal oxides. We have restricted ourselves to the above metals in their higher oxidation states, *i.e.* VI, V and IV for Mo and W and V and IV for V. Several results will be presented here, in the order of increasing complexity.

The simplest case is exemplified by the two-center system $V_2O_3Q_4^-$ first described by Sawyer (Q = hydroxy-8-quinolate anion). Unfortunately it does not display any mixed valence behaviour and we think this is due to the pecularities of its structure. This species can be obtained by reaction of $VO_2Q_2^-$ and VOQ_2 and it is believed that one of the oxygens of the *cis* VO_2 group of $VO_2Q_2^-$ fills the vacant position in VOQ_2; thus in the addition compound the two d_{xy} orbitals of the two vanadium atoms would have a zero overlap.

Tetranuclear systems $[W_4O_8Cl_8(H_2O)_4]^{2-}$, $[W_4O_8(NCS)_{12}]^{6-}$, $[W_4O_8(NCS)_4(C_2O_4)_4]^{6-}$ have been prepared and studied by X-Ray crystallography, ESR and ESCA. Linear W–O–W bridges and coplanar d_{xy} orbitals allow an easy interaction and mixed valence effects are observed, with very intense intervalence bands (ϵ up to 46,000) and electronic mobility observed by ESR. In the first compound, the rate of electron transfer has been estimated as *ca.* 10^8 sec^{-1} at –50 °C from ESR experiments.

It is possible to prepare hexanuclear systems, starting from isopolyanions such as $Mo_6O_{19}^{2-}$ and reducing by one electron, by electrolysis in an aprotic solvent. An ESR study of the brown $Mo_6O_{19}^{3-}$ ion has revealed a strongly trapped electron at the liquid nitrogen temperature. Hyperfine parameters show a very weak ground state delocalization, comparable to the one observed in $PMoW_{11}O_{40}^{4-}$ in which the molybdenum atom acts as an 'electron sink'. The intervalence band in $Mo_6O_{19}^{3-}$ appears as a weak shoulder near 9000 cm^{-1} on the edge of a more intense d–d band. This assignment is supported by the study of $MoW_5O_{19}^{3-}$.

With dodecanuclear systems, such as reduced $PMo_{12}O_{40}^{3-}$, the situation is more complicated since more than one type of junction between adjacent WO_6 octahedra can be found. In the $PMo_{12}O_{40}^{3-}$ structure, some junctions are the same as in $Mo_6O_{19}^{2-}$ but there are also junctions of a new type. They seem to be responsible of the much higher ground state delocalization observed in ESR and of the easier thermal mobility.

Finally the case of highly reduced polyanions, such as $H_2W_{12}O_{40}^{6-}$ reduced with 6n electrons (n = 1,2,3,4), shows the appearance of collective effects due to the great number of electrons introduced. Contrary to the first reduced species, it is now necessary to perform the reduction in a protic solvent. Protonation of outer oxygen atoms seems to play a role since an X-ray study of $Rb_4H_8[H_2W_{12}O_{40}]$ (*i.e.* $H_2W_{12}O_{40}^{6-}$ + $6e^-$ + $8H^+$) suggests marked differences in W–O bond lengths. In this structure, 3 tungsten atoms have moved by as much as 0.48 Å with respect to the original structure and it seems very likely that one among the four $W_3^{IV}O_{13}$ groups of the structure has become a $W_3^{IV}O_{13}$ group. The electron delocalization would occur inside this group only, rather than over the whole polyanion structure.

Work is in progress in order to correlate the extent of ground state delocalization in all these compounds with structural parameters, such as bond lengths and angles, determining the electronic interaction between metal centers.

High Spin–Low Spin Equilibrium in Six-Coordinate Cobalt(III) Complexes

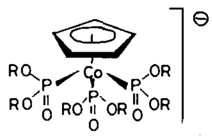
WOLFGANG KLÄUI*

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, F.R.G.

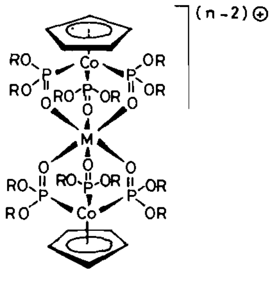
We have recently prepared the anionic complexes (1), R = CH_3, C_2H_5, $^iC_3H_7$. These diamagnetic half-sandwich complexes can act as symmetric tris-chelating *ligands* by using their P=O oxygen atoms. With metal ions M^{n+} (n = 2, 3) very stable complexes of the type $[\{(C_5H_5)Co[P(O)(OR)_2]_3\}_2M]^{(n-2)+}$ (*e.g.* (2)–(8)) are formed [1–4].

The cobalt(III) complexes (9), R = CH_3, C_2H_5, $^iC_3H_7$, have been obtained by electrochemical oxidation of the corresponding Co(II) compounds (2) at +1.3 V at a carbon gauze in CH_2Cl_2 [5]. These cationic species (9) (isolated as PF_6-salts) are *the first reported examples of octahedral d^6 Co(III) complexes exhibiting a high spin–low spin equilibrium.* The singlet–quintet spin transition has been followed by temperature dependent IR, ^1H- and ^{31}P-NMR spectroscopy, magnetic measurements, and cyclic voltammetry.

The compounds (9) have a dark green colour at room temperature which turns into light yellow upon cooling. The thermochromism is fuly reversible in the solid state as well as in solution, and it is paralleled by a strongly temperature dependent magnetic moment. The compound (9), R = C_2H_5, PF_6-salt, for example, shows a magnetic moment $\mu_{eff} \approx 0.4$ B.M. at 4.2 K and 4.1 B.M. at 393 K in the solid state [6].



(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).

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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.*