unpaired electron being in a π-orbital of d_{yz} character. There are several excited states with the same (doublet) and with higher (quartet) spin multiplicity as the ground state within a range of only a few multiples or less of the spin–orbit coupling constant ($\lambda_{Co} \approx -400\ cm^{-1}$) [1, 2].

Upon dissolution of the complex Co(saphen) (which was chosen because of solubility reasons) in coordinating solvents a crossing of states is observed. The ground state of the complex changes from $^2A_2$ to $^2A_1$. This change is due to coordination of a solvent molecule in axial position. The a_1 (d_{z^2}) orbital is becoming stronger σ-antibonding and it is consequently raised above the d_{yz} orbital whose energy is little affected by the axial coordination. Near the 'crossing' point strong mixing of $^2A_2$ and $^2A_1$ occurs because both states belong to the same irreducible representation of the double group, the closest approach of the two states being $\sqrt{3}\lambda$. ESR Parameters change drastically near this 'crossing' point. The electronic rearrangement induced by solvent interaction in these complexes is due to an accidental near degeneracy of the ground state, which is typical for low spin d^7 systems with square planar structure.

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Variable Electronic Properties of High Spin Cobalt(II)

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Octahedral high spin cobalt(II) is a well known example of electronic quasi degeneracy, since the ground $^4T_{1g}$ level of O_h symmetry is usually split to some extent by low symmetry components of the ligand field. ESR spectra are a very sensitive means for monitoring the nature of the distortions, because the g values are expected to vary dramatically according to which orbital component of $^4T_{1g}$ becomes the lowest energy state in the distorted field.

The theory necessary to understand the g and A values in octahedral and axial ligand fields was worked out by Abragam and Pryce [1], but it is an experimental result that often the actual symmetry is lower than axial and the principal directions of the spin hamiltonian tensors do not coincide with the 'molecular' axes [2].

Classic ligand field theory is not able to reproduce the experimental spin hamiltonian parameters which can be justified only using an Angular Overlap procedure we have developed [3], according to which both the principal values and directions of g and A can be obtained through a completely symmetry independent procedure. The main advantage of the Angular Overlap model, as compared to classic ligand field, is that it introduces parameters which reflect the σ and π nature of the bonding interaction. Further anisotropy in the π interaction is easily taken into account.

The versatility of the method has been checked on tetragonal octahedral complexes such as $Co(py)_4Cl_2$, $Co(pyz)_4Cl_2$, $Co(acac)_2L_2$ (py = pyridine; pyz = pyrazole; acac = 1,3-pentane-dione; L = pyridine, 6-methylquinoline, water). We were able to show that the g values and directions are mainly determined by the differences in the π ability of the axial and equatorial ligands.

The large variability of the electronic properties, as monitored by the spin hamiltonian parameters and their principal directions, is not a unique feature of octahedral complexes, and also tetrahedral and five-coordinate complexes show the same effects. In this case the ground orbital level is non degenerate. However spin–orbit coupling removes the spin degeneracy so that the two lowest Kramers doublets are quasi degenerate on the ESR experiment energy scale.

Examples will be provided for different geometrical distortions of the parent symmetries and attempts will be made to give general rules for using the ESR spectra as a structural tool for cobalt(II) complexes.

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Mixed Valence in Small and Big Polynuclear Entities having Metal–Oxygen–Metal-Bridges

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As a part of a research program on mixed valence compounds of Mo, W and V with oxygen bridges, we 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

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We have recently prepared the anionic complexes (1), R = CH_3, C_2H_5, $^{i}C_3H_7$. 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, $^{i}C_3H_7$, 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].