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