we wish that the experimentalists (of which we are) obtain useful informations on the complexes that it would be interesting to synthetize with the help of overlap density maps as those shown during the lecture. Such a map is schematized below for the case of a Cu(II) VO(II) heterobinuclear complex.

According to the available time, we intend to approach some of the following situations: (*i*) planar [1] and roof-shaped [2] hydroxo-bridged copper(II) dimers; (*ii*) heterobinuclear complexes in which the strict orthogonality of the magnetic orbitals is realized [3]; (*iii*) very strong antiferromagnetic coupling between transition ions far away from each other [4]; (*iv*) orbital reversal in copper(II) polynuclear complexes through the action of solvent molecules [5].

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Spin Crossover in Solid Solution

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The temperature dependent high spin (HS) ⇌ low spin (LS) transition, otherwise called spin crossover, has been well established for many first-row transition metal complexes, particularly for complexes of iron(II) [1]. The phenomenon has been observed mostly in the crystalline state, but also in solution. The spin crossover characteristics have been found to depend on various chemical influences, such as ligand substitution, the nature of the non-coordinating anion and the crystallizing solvent.

It has been shown by ^{57}Fe Mössbauer spectroscopy that the spin crossover behaviour in the solid solutions of $[Fe_xZn_{1-x}(2\text{-pic})_3]Cl_2\cdot EtOH$ (2-pic = 2-picolylamine) is also susceptible to metal dilution [2, 3]. At a given temperature, the HS state becomes favoured over the LS state with decreasing x. This may be qualitatively interpreted on the grounds of a cooperative domain model [2]. A phenomenological thermodynamic treatment [4] yields estimates of the changes of enthalpy and entropy as well as the domain size. A statistical model has also been successfully applied, which also allows to estimate the domain size and, in addition, an average effective frequency of the metal–ligand vibrational modes in each of the two spin states.

Mössbauer effect studies of the solid solution of $[Fe_xCo_{1-x}(2\text{-pic})_3]Cl_2\cdot EtOH$ show similar results. The relative stability of the HS state, at a given temperature, also increases with decreasing x. The $Fe_x/Co_{1-x}/2$-pic system, however, shows higher transition temperatures, at a given x, than the $Fe_x/Zn_{1-x}/2$-pic system, apparently due to the more rigid lattice of the former system.

The effect of metal dilution in solid solutions of $[Fe_xM_{1-x}(phen)_2(NCS)_2]$ (M = Co, Mn, Ni) as studied by Mössbauer spectroscopy [5] follows the same line: at a given temperature, the $^5T_2(O_h)$ state becomes favoured over the $^1A_1(O_h)$ state upon lowering x.

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Electron Transfer in Mixed-Valence Compounds

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In mixed-valence compounds where electronic interactions between metal sites are relatively weak,