Round Table: How much do we know about Metal–Metal Interactions?

Convener: DANTE GATTESCHI; Florence, Italy

K1

How Much do We Know about Metal–Metal Interactions?

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Clusters of metal ions are present in many metalloproteins and metalloenzymes, such as in several copper proteins, in hemocyanin, in hemerithrin, in iron–sulphur proteins, in cytochrome *c* oxidase, *etc.* In all these cases the metal ions are interacting in such a way that the electronic structure of the cluster differs appreciably from the sum of the electronic structures of the individual metal ions. When it occurs we may say that metal–metal interactions are operative. We will be interested in this round table to interactions between paramagnetic ions which are easily monitored through measurements which are sensitive to the magnetic properties of the cluster and to mixed valence interactions which occur when the same metal is present in two different oxidation states. The topics which will be covered will be the fundamental theory underlying the mechanism of exchange interactions which determine magnetic coupling in metal clusters, the strategy for the development of synthetic model compounds for dinuclear and polynuclear metal sites in metalloproteins, a survey of experimental data on the interactions between metal ions separated by single atom and polyatomic bridges, including mixed valence interactions, exchange interactions on tetranuclear copper(II) complexes, and magnetic resonance spectra of exchange coupled systems.

For the last topic the attention will be focussed on oligonuclear clusters, *i.e.* on systems involving 2, 3 and 4 similar or dissimilar metal ions. The EPR parameters of the cluster will be related to those of the individual metal ions in the assumption of substantial isotropic coupling and the theoretical expectations will be compared with experimental data.

The role of anisotropic and antisymmetric exchange on the EPR spectra of metal clusters will also be discussed. In a series of dinuclear complexes it will be shown how these terms, which are usually smaller than the isotropic term, may influence the g and D values and divertions, and how it is possible to correlate the exchange interactions involving one ion in the ground state and the other in the excited state with structural and electronic parameters.

Finally a brief mention will be made of the NMR spectra of dinuclear metal complexes, showing how the proton isotropic shifts and longitudinal relaxation time are influenced by the presence of two metal ions.

K2

Mechanism of the Interaction between Metallic Centers: Concepts and Experimental Results

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We propose a model of the interaction between the metallic centers of a polymetallic system which permits not only the rationalization of most of the results already known, but also the design of new systems exhibiting expected properties. If we consider a copper(II) dimer, the interaction leads to two low lying states, a spin singlet and a spin triplet, separated by J. The interaction is said to be antiferromagnetic if the spin singlet is lower in energy ($J < 0$). It is said to be ferromagnetic in the opposite case ($J > 0$). In our model, the energy gap J is the algebraic sum of two components, J_{AF} and J_F, favoring the antiferro- and the ferromagnetic situations respectively. In some way, the sign and the magnitude of J result from the opposition between two fighters. These fighters, as the gladiators, have not the same tools. The tools of the antiferromagnetic gladiator are the overlap S between the *magnetic orbitals* and the energy gap Δ between the molecular orbitals built from the magnetic orbitals. The tool of the ferromagnetic gladiator is the two-electron exchange integral C between the magnetic orbitals:

$$J = J_{AF} + J_F$$

$$J_{AF} = -2\Delta S$$

$$J_F = -2C$$

The concept of magnetic orbital will be specified.

The antiferromagnetic gladiator is generally more efficient than his component. This is particularly true when the metallic centers are largely separated (more than *ca.* 4 Å). We shall show how it is possible to *tune* the efficiency of the tools of the antiferromagnetic gladiator in a given bridging network, by playing on the nature of the terminal ligands. We shall emphasize that the interaction may be very large even when the