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

Convener: DANTE GATTESCHI; Florence, Italy

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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 metallic centers are far away from each other. Some new bridging ligands particularly appropriate for transmitting electronic effects over long distances will be presented.

In some quite peculiar cases, it is possible to annihilate the trenchant of the tools of the antiferromagnetic gladiator, by realizing the orthogonality of the magnetic orbitals. *J* is then positive and the ground state is the state of highest spin multiplicity. This orthogonality can be strict or accidental. Examples corresponding to both situations will be presented. In this respect, the extraordinary versatility of the azido bridging ligand in stabilizing either the singlet state or the triplet state in copper(II) dimers will be pointed out.

In conclusion, the relevance of our work to the study of the polymetallic sites in biological systems will be discussed.

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K3

Interactions between Metals Separated by Single Atom Bridges

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For a wide variety of dimeric and polymeric complexes in which the paramagnetic metal centers are linked by one or more single atom bridges, it is well established that the magnetic properties are in large part determined by the structure of the bridging unit. The precise nature of this magneto-structural correlation, which would in principle allow the use of magnetochemistry as a proble of molecular structure in complex biomolecules, continues to be the subject of intense research activity.

While data exist for complexes of many metal ions, the majority of the data are for two related systems. In what may be both synthetically and magnetically the simplest case, that of the copper(II) dimers $[L_2CuOH]_2$ in which the copper centers are bridged by two hydroxo groups, early results from our laboratory and elsewhere suggested that a linear correlation exists between the isotropic ground state exchange coupling parameter (J) and the Cu–O–Cu bridging angle (ϕ). This general concept was supported by a simple qualitative MO description, and subsequently by semi-quantitative calculations based on EHT and AOM formalisms. Recent work involving more complex structures, however, has demonstrated that the original correlation obtains for only a limited subset of possible structures, and that the complete expression relating J to structural parameters includes other angular deformations.

In the case of chromium(III), the complexes most extensively studied are again the di-hydroxo bridged 'species. In addition, however, the singly bridged rhodo and erythro complexes and their analogues, which can exist in equilibrium with the doubly bridged systems, have also been studied in detail. Early work focussed on the relationship between J and ϕ, in analogy with the copper(II) result, and it was soon apparent that no linear relationship exists. However, a simple qualitative view of this system suggests that the observed results are broadly consistent with the expected correlation. More recent work has shown that the Cr–O distance R is of significance, and a correlation between J and ϕ/R has been suggested.

Two separate groups have stressed the significance of a third structural parameter, the dihedral angle θ between the O–H vector and the Cr_2O_2 bridging plane. The importance of this has been established by studies on alkoxo-bridged systems, and by single crystal spectroscopic investigations of related series of complexes of this type. This work has led to the formulation of a model for J which includes terms in R, θ, and ϕ.

The results obtained with other metal ions and other structural types, while less extensive than these, are consistent with the pattern which has emerged from the copper and chromium studies.

K4

Magnetic Exchange Interactions Propagated by Polyatomic Bridges

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The investigation of the mechanisms of electron transfer at long distances is one of the crucial problems in bioenergetics. The fundamental nature of electron transfer between transition metal ion sites in both electron-transfer proteins and precursor complexes for outer- and inner-sphere redox reactions needs to be determined. In order for electron transfer to occur between two transition metal ions that are well separated, there has to be an electronic interaction between the two metal ions. This interaction