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