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.

- O. Kahn and M. F. Charlot, *Nouv. J. Chim., 4,* 567 (1980).
- O. Kahn, J. Galy, J. Journaux, J. Jaud and I. Morgenstern-Badarau, *J. Am. Chem. Soc., 104,* 2165 (1982).
- I. Morgenstern-Badarau, M. Rerat, O. Kahn, J. Jaud and J. Galy, *Inorg. Chem., 21,* 3050 (1982).
- J. Commarmond, P. Plumere, J. M. Lehn, Y. Agnus, R. Louis, R. Weiss, O. Kahn and I. Morgenstern-Badarau, *J. Am. Chem. Soc., 104,* 6330 (1982).

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 would be propagated by the organic material that is bridging between the two metal ions. In a binuclear complex of paramagnetic metal ions bridged by an organic species the electronic interaction that develops between the two metal ions is called a magnetic exchange interaction.

There are at least four instances where polyatomic bridges propagated magnetic exchange interactions: (1) Polynuclear transition metal complexes with unsaturated bridges; (2) Polynuclear transition metal complexes with saturated bridges; (3) Transition metal complexes with a paramagnetic ligand; and (4) Organic biradicals. Emphasis will be placed on the first two cases, where unsaturated polyatomic bridges include imidazolate, pyrazine, oxalate, cyanurate and aromatic diamines and saturated bridges are represented by dabco and various aliphatic dicarboxylate dianions.

The distance dependence of magnetic exchange interactions will be examined. It will be shown that there is no simple distance dependence. Exchange interactions can be propagated over large distances. For example, hydrogen-bond interactions between metal complexes can propagate exchange interactions; temperature dependence in the exchange parameter J has been seen for some of these complexes by means of the observation of singlet-to-triplet EPR transitions.

The relationship between magnetic exchange interactions propagated by extended polyatomic bridges and electron transfer via these same bridges will be discussed. The study of well characterized, generally binuclear, mixed-valence transition metal complexes is proving to be useful in characterizing the factors controlling electron transfer between metal ions. Magnetic exchange interactions are present in certain mixed-valence complexes, such as the trinuclear oxo-centered $Fe_2^{III}Fe^{II}$ carboxylate complexes.

K5

Strategies in the Development of Synthetic Model Compounds for Dinuclear and Polynuclear Metal Sites in Metalloproteins

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Many of the known metalloproteins and metalloenzymes contain more than one metal ion at the active site. The metal ions can be relatively close together (with a bridging ligand in between them), or separated over more than 5–6 Å. This paper will only deal with the first category. The ligand-bridged dinuclear or polynuclear centers can either be homopolyatomic (such as the copper dimers in hemocyanin [1] and the iron tetramers [2] in ferredoxin), or heteropolyatomic (such as the Cu–Zn site in bovine syperoxide dismutase [3], the Fe and Mo-containing cofactor in nitrogenase [4], and the Cu–Fe site in cytochrome *c* oxidase [5]). In some cases, such as in the iron–sulfur proteins, the polynuclear coordination entity can be extracted from the proteins, without decomposition [6].

In developing strategies for the synthesis of low-molecular weight analogs for these dinuclear and polynuclear metal sites, two approaches can be followed, *i.e.*:

(a) Use of small ligands that are well known to form bridges between two (or more) metal ions. Examples are OH^- (for Cu dimers) [7], S^{2-} (for iron–sulfur clusters) [8] and deprotonated imidazole (for copper dimers) [9]. Under these circumstances dinuclear or polynuclear metal units can only be formed in certain cases, and generalisations are difficult to make.

(b) Use of binucleating (or polynucleating) chelating ligands to hold two (or more) metal ions bound to the same ligand [10]. In addition small bridging ligands, such as OH^-, may be present. These systems may or may not contain a ligand atom bridging two or more metal ions. Asymmetric binucleating chelating ligands can be designed to synthesize asymmetric dimers, which may even hold two different metal ions [11]. Steric constraints and/or intramolecular interactions (*e.g.* hydrogen bonding) can be used to generate a certain coordination geometry, or to regulate metal–ligand distances [12].

The most successful results have been obtained so far, when method (b) was used. However, many clusters have also been prepared according to method (a). The present paper will mainly deal with nitrogen (amine, imidazole) and oxygen (phenolate, alcoholate) as ligand donor atoms in binucleating and polynucleating chelating ligands. Special attention will be given to ligand systems accessible via relatively simple synthetic methods. The formation of the dinuclear and polynuclear coordination compounds, their molecular structures, and their chemical and spectroscopic properties will be discussed in detail for a few selected systems.

1 C. D. Garner and P. M. Harrison, *Chem. in Britain, 18,* 1 (1982).
2 W. Lovenberg (ed.), 'Iron–Sulfur Proteins', Vol. III, New York (1977).
3 J. S. Richardson, K. A. Thomas, B. H. Rubin and D. C. Richardson, *Proc. Natl. Acad. Sci. USA, 72,* 1349 (1975).
4 V. K. Shah and W. J. Brill, *Proc. Natl. Acad. Sci. USA, 78,* 3438 (1981).
5 L. Powers, B. Chance, Y. Ching and P. Angiolillo, *Biophys. J., 34,* 465 (1981).
6 R. H. Holm, *Chem. Soc. Rev.,* 455 (1981), and references cited there.