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

JAN REEDIJK

Department of Chemistry, Gorlaeus Laboratories, State University Leiden, P.O. Box 9502, 2300 RA Leiden, The Netherlands

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.

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K6

Binucleating Ligands for Probing Metal–Metal Interactions in Hemocyanin and Cytochrome Oxidase Models

CHRISTOPHER A. REED*, NIGEL G. LARSEN, BRIAN S. ERLER, VICKIE McKEE, JEFFREY V. DAGDI-GIAN and ROBERT BAU
Chemistry Department, *University of Southern California, Los Angeles, Calif. 90089-1062, U.S.A.*

Interest in multimetal metalloproteins frequently results from the observation of spin coupling phenomena because they give clues to the presence of proximate paramagnetic centers. It is not usually the spin coupling *per se* that is important to the biochemistry of a metalloprotein but an understanding of the nature of the spin interaction is inextricably associated with the deduction of the structure of the metal sites. And it seems that the more completely the normal magnetic signatures of a metal are erased by spin coupling, the more challenging becomes the elucidating of structure. The diamagnetism of copper(II) hemocyanin derivatives and the EPR silent heme a_3–copper site of cytochrome oxidase are cases in point. The interrelationship of spin coupling and structure has dictated that progress in understanding magnetic interactions has been dependent on a detailed knowledge of structure, usually gained from X-ray crystallography. So it is, with the synthetic model compound approach to metalloproteins, that the design and synthesis of complexes which are amenable to definitive structural characterization is critically important. In this paper, the design, synthesis and structural characterization of spin coupled models for hemocyanin and cytochrome oxidase are discussed within the context of using magnetic coupling phenomena to draw structural implications for their binuclear active sites.

We have recently reported [1] an azide/alkoxide dibridged binuclear copper(II) complex which, like hemocyanin, is diamagnetic (Fig. 1, X = N_3). The rationale for understanding this strong antiferromagnetic coupling is based on a superexchange pathway via the bridging ligands for orbital overlap of the $(d_{x^2-y^2})^1$ ground states of the approximately tetragonal copper centers. In contrast, the trigonal bipyramidal copper centers in the corresponding acetate complex (Fig. 1, X = OAc) are essentially spin free (μ = 1.83 per Cu). These complexes endorse the proposal that diamagnetism in oxy- and methemocyanin (and Type III copper) is the result of dibridged tetragonal copper(II) centers with at least one O-bridged ligand such as alkoxide.

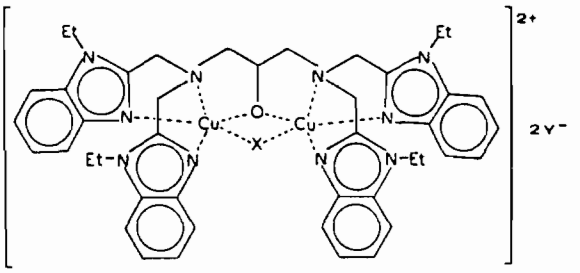

Fig. 1.

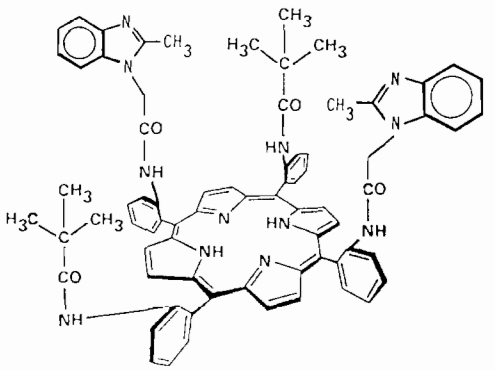

Fig. 2.

The most popular explanation for the absence of an EPR signal for the active site of resting state cytochrome oxidase is spin coupling between high-spin ferric heme a_3 and a proximate copper(II) center [2]. Figure 2 illustrates a ligand whose complexes with iron(III) in the porphyrin base and copper(II) coordinated in the bisbenzimidazole superstructure yield isolable crystalline materials of analytical and spectroscopic purity. Their magnetic properties are under investigation.

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