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Magnetic Coupling and ^{1}H NMR Spectroscopy of Binuclear Copper(II) Complexes

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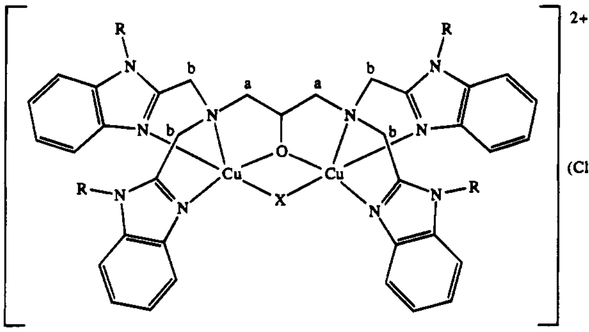
^{1}H NMR spectroscopy is not generally viewed as a viable solution characterization technique for paramagnetic copper(II) complexes, because slow electronic relaxation leads to broad resonances.[1] However a few reports have described copper(II) complexes that produce narrow ^{1}H NMR resonances.[2-11] The copper(II) complexes which produce such ^{1}H NMR spectra involve two paramagnetic centers which produce effective relaxation mechanisms. In most cases these are binuclear copper(II) complexes with moderate antiferromagnetic coupling ($2J$ values ranging from -156 to -545 cm^{-1}).[2,4-11] Here we report ^{1}H NMR spectra of binuclear copper(II) complexes in which variation of a bridging ligand causes a marked change in the magnetic coupling.[12] For these a quantitative relationship exists between the chemical shifts and the magnetic coupling over a wide range ($2J = +26$ to -1100 cm^{-1}) of coupling constants.

The (μ-alkoxo)(μ-X)dicopper(II) complexes [Cu_2(L-R)(X)](ClO_4)$_2$, **1**, were prepared both by an indirect method (A) as reported by Reed and co-workers[12] and by a new direct *in situ* approach (method B). In method A ethanolic solutions of the free ligand, HL-R (0.45 mmol), and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.90 mmol) were mixed to produce the unbridged complex [Cu_2(L-R)(H_2O)$_x$](ClO_4)$_2$ (**2**). Complex **2** was then reacted with **1** equiv of NaX to produce the bridged species. In the new method (B) the free ligand, HL-Me (0.45 mmol), and $Cu(ClO_4)_2 \cdot 6H_2O$ (0.90 mmol) were added sequentially as solids to boiling methanol. Addition of a methanol solution containing **2** equiv of NaX precipitated the desired bridged complex. The crude solids were collected, washed with cold alcohol, and recrystallized from acetonitrile with vapor diffusion of diethyl ether. The structural characteristics both of [Cu_2(L-Me)(O_2CCH_3)](ClO_4)$_2$, which is analogous to [Cu_2(L-Et)(O_2CCH_3)](ClO_4)$_2$,[12] and of [Cu_2(L-Me)(pz)](ClO_4)$_2$, with a pyrazolate bridge in place of the acetate ligand, have been determined by X-ray crystallography.



1, [Cu(L-R)(X)](ClO_4)$_2$

The ^{1}H NMR spectra of [Cu_2(L-Me)(O_2CCH_3)](ClO_4)$_2$, [Cu_2(L-Me)(O_2N)](ClO_4)$_2$, and [Cu_2(L-Me)(N_3)](ClO_4)$_2$ in acetonitrile-d_3 solutions at 23 °C are shown in Figure 1. Reasonably sharp, isotropically shifted signals are observed over the 250–1.5 ppm chemical shift range for [Cu_2(L-Me)(O_2CCH_3)](ClO_4)$_2$.

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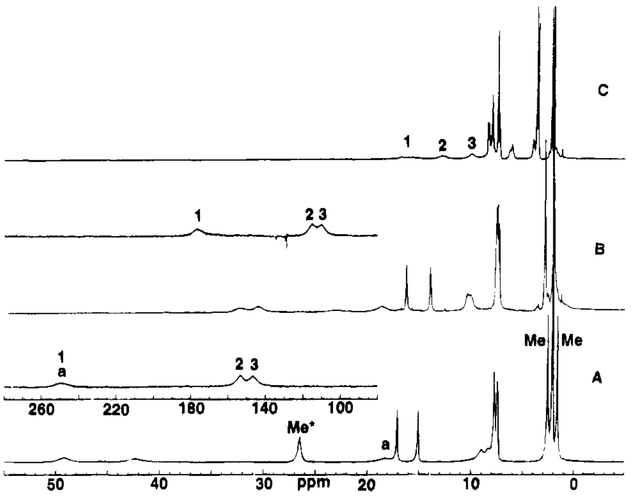

Figure 1. 300-MHz ^{1}H NMR spectra of (A) [Cu_2(L-Me)(O_2CCH_3)](ClO_4)$_2$ (−5 to 55 ppm; 100 to 280 ppm, inset), (B) [Cu_2(L-Me)(O_2N)](ClO_4)$_2$ (−5 to 55 ppm; 100 to 280 ppm, inset); and (C) [Cu_2(L-Me)(N_3)](ClO_4)$_2$ (−5 to 55 ppm) in acetonitrile-d_3 at 23 °C. In trace A, resonance labels are as follows: Me, methyl groups of L-Me; Me*, methyl group of the acetate ligand; a, methylene group a.

For [Cu_2(L-Me)(O_2N)](ClO_4)$_2$, the spectrum is qualitatively similar to that of the acetate complex with a narrowed spectral width that extends only over the 180−1.5 ppm range. On the other hand, the solution spectrum of [Cu_2(L-Me)(N_3)](ClO_4)$_2$ (Figure 1C) is dramatically condensed.

The assignment of the resonances in the spectrum of [Cu_2(L-Me)(O_2CCH_3)](ClO_4)$_2$ has been accomplished through consideration of relative peak areas and the use of selective deuteration. The resonances at 1.57, 2.52, and 26.47 ppm integrate to 6:6:3 protons and can be assigned to the two types of benzimidazole methyl groups and the acetate protons, respectively. Spectral observation of [Cu_2(L-Me)(O_2CCD_3)](ClO_4)$_2$ (prepared from sodium acetate-d_3) confirms the assignment of acetate resonance. Other resonances were identified through the use of HL-Me-d_{24}. This labeled ligand was prepared by heating 1,3-diamino-2-propanol-*N,N,N′,N′*-tetraacetic acid and 4 equiv of *N*-methyl-1,2-diaminobenzene in 6 N DCl under reflux for 24 h. Under these conditions, the methylene groups (b) are labeled with deuterium, and because of the ease of exchange of the protons of the aromatic diamine under an acidic reflux,[13] the resulting benzimidazole groups are also labeled with deuterium. In the ^{1}H NMR spectrum of [Cu_2(L-Me-d_{24})(O_2CCH_3)](ClO_4)$_2$ the two resonances at 18.21 and 248.5 ppm retain their full intensity (integration 2:2) and can be assigned to the methylene protons (a). The resonance for the single methine group (expected to be the most downfield shifted) is not observed presumably due to line broadening. Integration of the remaining resonances whose intensities vanish when L-Me-d_{24} was used accounts for the remaining 24 protons, but identification of specific resonances was not possible. However, it is clear that the solution spectrum is consistent with the solid state structure of [Cu_2(L-Me)(O_2CCH_3)](ClO_4)$_2$. In contrast to the observations of Balch *et al.*[3] and Holz *et al.*[4] in which dipolar relaxation was proposed to be the dominant proton relaxation mechanism, there appears to be no correlation between isotropic shift and line width for [Cu_2(L-Me)(O_2CCH_3)](ClO_4)$_2$. Thus multiple relaxation mechanisms may be determining the line widths.

The general trend in the isotropically shifted resonances to more upfield values (Figure 1) within the group, [Cu_2(L-Me)(O_2CCH_3)](ClO_4)$_2$, [Cu_2(L-Me)(O_2N)](ClO_4)$_2$, and [Cu_2(L-Me)(N_3)](ClO_4)$_2$, can be correlated with the magnetic coupling within these dimers. Figure 2 shows plots of the chemical shifts at 23 °C for three resonances of each complex versus the *J* values obtained from solid state measurements for the acetate-, nitrite-, and azide-bridged complexes.[12] The solid curve was calculated from the Bleaney−Bowers expression (eq 1) that

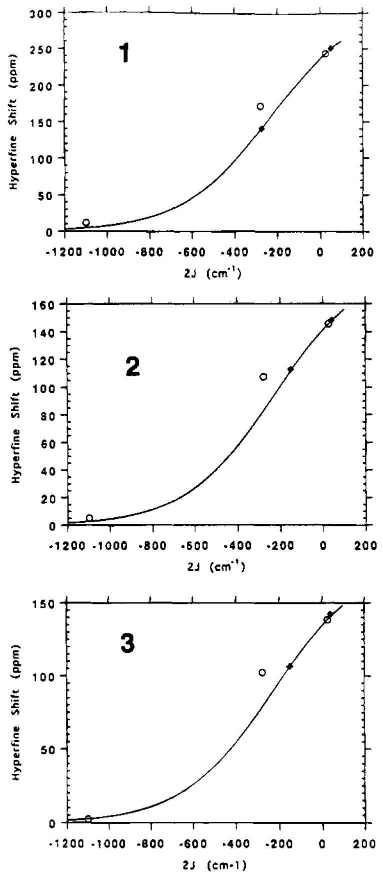

Figure 2. Chemical shifts at 23 °C of the resonances labeled 1, 2, and 3 in Figure 1 as a function of the *J* values.[12] Open circles are the experimental data. The solid curve was calculated by using the Bleaney−Bowers expression.

$$\chi_m = (2Ng^2b^2/kT)[1 + {}^1/_3\exp(-2J/kT)]^{-1} \qquad (1)$$

relates the molar susceptibility, χ_m, and the magnetic coupling constant, *J*.[14] The derivation of this curve assumes proportionality between χ_m and the chemical shift and uses the acetate-bridged complex to scale the data. Reasonable agreement between theory and experiment exists over a fairly wide range of magnetic coupling parameters. From this plot we can estimate coupling constants of compounds for which magnetic data are unavailable. For the pyrazolate- and formate-bridged complexes $2J$ is estimated as −360 and +40 cm^{-1}. Similar correlations between χ_m and the chemical shift have been observed for dinuclear iron complexes.[15]

The ^{1}H NMR spectra of these complexes should be useful in monitoring chemical reactions. In Figure 3 we show an application that involves an examination of the purity of the complexes that are obtained from the two synthetic schemes outlined above. The ^{1}H NMR spectra of [Cu_2(L-Me)(O_2CCH_3)](ClO_4)$_2$ prepared by methods A and B are shown in

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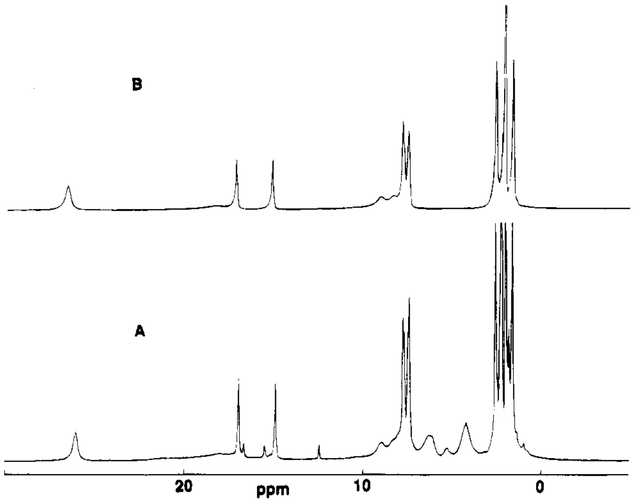

Figure 3. Portion of the 300-MHz ^{1}H NMR spectra of two samples of $[Cu_2(L\text{-}Me)(O_2CCH_3)](ClO_4)_2$ in acetonitrile-d_3 at 23 °C: (A) sample prepared by method A; (B) a sample prepared by method B.

Figure 3. When $[Cu_2(L\text{-}Me)(O_2CCH_3)](ClO_4)_2$ was prepared by method A,[12] resonances due to impurities, particularly in the 0−15 ppm region, were observed (trace A) and recrystallization is not effective in removing these impurities. These impurity resonances are absent from the spectrum of the complex when it is prepared via the new method (B).

In summary, ^{1}H NMR spectroscopy has been shown to be applicable to characterization of the structure and reactivity of binuclear copper(II) complexes with magnetic coupling that ranges from weakly ferromagnetic to strongly antiferromagnetic.

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Supplementary Material Available: A drawing of $[Cu_2(L\text{-}Me)(pz)](ClO_4)_2$, text giving the ligand synthesis, and tables of crystal structural parameters and refinement data, atom coordinates, bond distances and angles, hydrogen coordinates, and anisotropic thermal parameters (12 pages). Ordering information is given on any current masthead page.

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