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Halide and Hydroxide Linearly Bridged Bimetallic Copper(II) Complexes: Trends in Strong Antiferromagnetic Superexchange Interactions

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Supporting Information

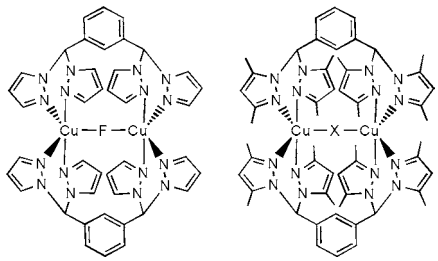
ABSTRACT: Centrosymmetric $[Cu_2(\mu\text{-}X)(\mu\text{-}L_m^*)_2](ClO_4)_3$ (X = F^-, Cl^-, Br^-, OH^-, L_m^* = *m*-bis[bis(3,5-dimethyl-1-pyrazolyl)methyl]benzene)], the first example of a series of bimetallic copper(II) complexes linked by a linearly bridging mononuclear anion, have been prepared and structurally characterized. Very strong antiferromagnetic exchange coupling between the copper(II) ions increases along the series $F^- < Cl^- < OH^- < Br^-$, where $-J$ = 340, 720, 808, and 945 cm^{-1}. DFT calculations explain this trend by an increase in the energy along this series of the antibonding antisymmetric combination of the p orbital of the bridging anion interacting with the copper(II) d_{z^2} orbital.

One of the dominant themes in transition metal chemistry, for more than 50 years, has been the magnetic superexchange interactions of bimetallic complexes where the two metals are bridged by small ligands.[1] Extensive work has shown that magnetic exchange between two metals correlates with the type and geometry of the metal centers and the bridging ligands. The study of magnetic exchange interactions is fundamentally important;[2] it impacts materials science[3] and the active sites of several metalloenzymes.[4] The magnetic properties of dinuclear copper(II) systems are of particular interest because the d^9 configuration of each copper(II) ion involves only one magnetic orbital in the exchange pathway.[5]

The simplest possible linking arrangement between two metals is a linear mononuclear anionic bridge (M−X−M). Despite the simplicity, this arrangement is virtually unstudied, to date, because very few compounds of this type have been prepared.[6,7] We have recently designed and prepared third generation bis(pyrazolyl)methane ligands that support the syntheses of bridged dinuclear metallacycles where the metals are held in fairly close proximity, an arrangement perfectly suited to form these types of complexes. In our initial work with the ligand *m*-bis[bis(1-pyrazolyl)methyl]benzene, L_m, we showed that the cation in $[Cu_2(\mu\text{-}F)(\mu\text{-}L_m)_2](BF_4)_3$ has a linear or nearly linear (solvate dependent) Cu−F−Cu central core (Scheme 1) and observed a strong antiferromagnetic interaction, J = −365 cm^{-1}.[7b]

We have now prepared the new ligand *m*-bis[bis(3,5-dimethyl-1-pyrazolyl)methyl]benzene (L_m^*) and show here that it is superior for fundamental studies in this area because it maintains the same structural type (Scheme 1) and enforces the linearity of the bridging group. Importantly, we have been able to use this ligand to synthesize a series of structurally similar copper(II) metallacycles with different bridging anions. Specifically, we report here the syntheses of the complexes $[Cu_2(\mu\text{-}X)(\mu\text{-}L_m^*)_2](ClO_4)_3$, where X = F^-, Cl^-, Br^-, and OH^-. These complexes represent the *first series of bimetallic complexes with a linear Cu(II)−X−Cu(II) bridging arrangement.* We are particularly interested in the magnetic and EPR properties of these complexes because previous work[1,2] indicated that linear Cu−X−Cu units yield complexes that show strong intramolecular antiferromagnetic superexchange interactions, but very few complexes of this type had been prepared previously. Thus, these new complexes allow the first study of intramolecular antiferromagnetic superexchange interactions of linearly bridged copper(II) ions and the determination of the *impact of changing the mononuclear bridging group* while holding the structure constant (except Cu−X bond lengths).

Scheme 1. Schematic Drawing of the Cations $[Cu_2(\mu\text{-}F)(\mu\text{-}L_m)_2]^{3+}$ and $[Cu_2(\mu\text{-}X)(\mu\text{-}L_m^*)_2]^{3+}$



A homologous series of linearly bridged, cationic metallacycles with perchlorate as the counterion was prepared as follows: for $[Cu_2(\mu\text{-}F)(\mu\text{-}L_m^*)_2](ClO_4)_3$ (**1**), by anion exchange of $[Cu_2(\mu\text{-}F)(\mu\text{-}L_m^*)_2](BF_4)_3$ (formed[7] by fluoride abstraction from BF_4^-); for $[Cu_2(\mu\text{-}Cl)(\mu\text{-}L_m^*)_2](ClO_4)_3$ (**2**) and $[Cu(\mu\text{-}Br)(\mu\text{-}L_m^*)_2](ClO_4)_3$ (**3**), by the direct reaction of the building blocks of the metallacyle; and for $[Cu_2(\mu\text{-}OH)(\mu\text{-}L_m^*)_2](ClO_4)_3$ (**4**), by deprotonation of the water of

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crystallization in $Cu(ClO_4)_2 \cdot 6H_2O$ with Et_3N in the presence of L_m*. The molecular structures of **3** and **4**, as determined by X-ray diffraction, are shown in Figure 1; compounds **1** and **2** have

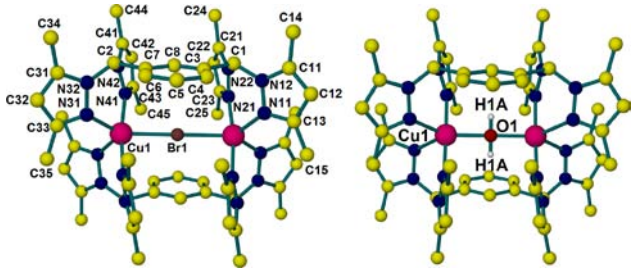

Figure 1. Structures of the cationic units of $[Cu_2(\mu\text{-Br})(\mu\text{-}L_m^*)_2](ClO_4)_3$ (**3**, left) and $[Cu_2(\mu\text{-OH})(\mu\text{-}L_m^*)_2](ClO_4)_3$ (**4**, right).

similar structures, and the numbering scheme in Figure 1 is correct for all four compounds. All four structures are centrosymmetric, with the inversion center at the linearly bridging anion. For complex **4**, the hydroxide hydrogen atom (which was located in a crystallographic difference map) is disordered equally across the inversion center with the unusual Cu−O−H angle of 90°. The geometry around the metal centers is distorted trigonal bipyramidal. The anion X, N11 and N31 are in the equatorial positions, while N21 and N41 are in the axial positions. The trigonal bipyramidal geometry is distorted toward a square pyramidal geometry; the τ_5 values[8] are between 0.64 and 0.70 (perfect TBP = 1, SP = 0). In line with previous data on d^9 copper(II) systems,[9] the axial M−N bond lengths are shorter than the equatorial M−N bond lengths (Table S2) by 0.10−0.27 Å. Steric factors related to the two L_m* ligands that form the metallacycle stabilize this axially compressed trigonal bipyramid over the more frequently observed axially elongated square pyramid.[9] The large axial compression is also explained in terms of the pseudo-Jahn−Teller (PJT) effect.[10]

The average M−N bond lengths remain relatively constant for the four complexes, and the Cu−X bond lengths increase as the size of the bridging anion increases, Table 1 and Figure S1. The ligands appear to have a moderating effect on the changes in the Cu−X bond lengths, where the fluoride and hydroxide lengths are slightly longer than predicted and the chloride and bromide noticeably shorter than predicted.[11]

The magnetic data, Figure 2, demonstrate very strong antiferromagnetic exchange coupling between the copper(II) ions. The Bleaney−Bowers equation derived from the Hamiltonian $H = -JS_1 \cdot S_2$ was applied to determine exchange integrals J (Table 2) from the high-temperature data (above 50 K, see SI). Antiferromagnetic exchange interactions were found to increase in the sequence $F^- < Cl^- < OH^- < Br^-$, where for Br^- and even OH^- the interaction is so strong that the compounds are nearly diamagnetic at room temperature.

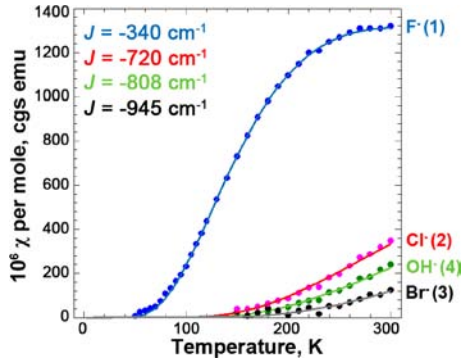

Figure 2. Dots: experimental magnetic susceptibility with the monomer impurity contribution subtracted. Lines: calculated with J values shown.

Table 2Experimental and Calculated (Broken Symmetry DFT) Spin Hamiltonian Parameters

complex	1	2	3	4
$-J$, cm^{-1}	340(5)	720(10)	945(20)	808(10)
$-J$ from DFT, cm^{-1}	380	914	1304	994
g_x	2.15[a]	2.183[b]	2.15[c]	2.122[b]
g_y	2.33	2.246	2.15	2.311
g_z	2.01	1.999	1.99	2.020
$\|D\|$, cm^{-1}	0.178	0.182	0.25	0.234
$\|E\|$, cm^{-1}	0.093	0.047	0.06	0.146
$D_{dipolar}$[d]	−0.030	−0.032	−0.024	−0.049

[a]X-band, 150 K. [b]High-field EPR, 305 K. [c]Q-band, 295K. [d]Calculated, point-dipole approximation.

"Broken symmetry" DFT calculations were performed to estimate the exchange integrals.[12] Simplified structures were used in which all atoms were retained at their X-ray positions, but the benzene rings as well as CH_3 groups were removed. As reported elsewhere,[13] the calculations seriously overestimate the magnitude of J (Table 2) but reproduce very well the experimental trend observed in the series of bridges. As indicated earlier by Hoffmann et al.,[2a] when the geometry about the metal is trigonal bipyramidal with the bridging group in the equatorial "*xy*" plane, the valence p orbital of the bridging group interacts more strongly with the magnetic d_{z^2} orbital in the antibonding antisymmetric combination (Figure 3) than the lower lying s orbital in the symmetric combination, raising the energy of the antisymmetric orbital, thus stabilizing the singlet state. Our calculations show that as one goes down the halide group the energy of both the symmetric and antisymmetric combinations increases (Table S4), indicating a stronger interaction, but the impact is greater for the higher energy antibonding combination, increasing the separation of the orbitals and consequently the magnitude of J.[2a] These trends are also borne out by the overlap integrals between the magnetic orbitals, which are 0.125, 0.186, 0.203, and 0.228 for

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1−4

complex·solvent	T, K	Cu−X−Cu angle, deg	Cu−X distance, Å	predicted Cu−X distance, Å[a]	average Cu−N distance, Å	τ_5[b]	Cu···Cu distance, Å
1·$2H_2O$	100	180	2.0227(2)	1.935	2.0702	0.70	4.0454
2	295	180	2.3308(4)	2.460	2.0410	0.70	4.6616
3·$2CH_3CN$	100	180	2.4733(3)	2.610	2.0334	0.64	4.9466
4·$2H_2O$	150	180	2.0230(3)	1.970	2.0882	0.68	4.0460

[a]Ref 11. [b]Calculated according to ref 8.

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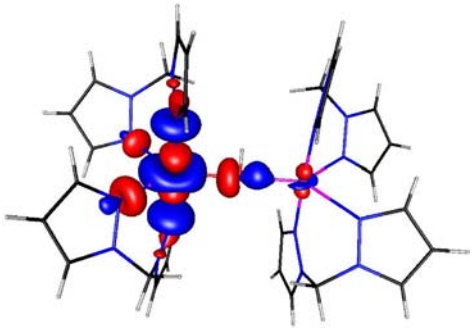

Figure 3. The magnetic orbital of one Cu(II) in **4** showing the d_{z^2} character, calculated using the broken symmetry approach.

the F^-, Cl^-, OH^-, and Br^- bridges, respectively. These integrals have been shown by theory to trend with J values.[1a] The calculations also show that the reduced spin density on the copper(II) d_{z^2} orbital decreases, and those on the halide group p_x orbital increase (the hydroxide is also larger than the fluoride), as the measured antiferromagnetic exchange interactions increase.

The magnitudes of the J values is particularly surprising, given that the geometry of complexes **1**−**4** has the interaction being transmitted through overlap of the "doughnut" portion of the magnetic d_{z^2} orbital (Figure 3). Large $-J$ values have been observed previously when a bridging group with relatively large Cu−X−Cu angles overlaps with the magnetic $d_{x^2-y^2}$ orbital in square planar or pyramidal geometry or along the z axis of a trigonal bipyramid.[1c] For the one known complex with a linear bridge, a bridge located similarly to those reported here, $[Cu_2(tet\text{-}b)_2Cl](ClO_4)_3$, the $-J$ value was reported to be 288 cm^{-1},[6a] substantially smaller than the 720 cm^{-1} value we observe for the Cl^- bridged **2**.

The triplet-state (S = 1) EPR spectra show unique features related to the structural design of the system (Figures S3−S5). The EPR parameters for these low symmetry copper(II) coordination spheres, idealized C_{2v}, were 'non-axial' with very anisotropic, rhombic g tensors and large E parameters compared to D. One of the g tensor components was very close to 2, a value consistent with the observed copper(II) coordination geometry resulting in the d_{z^2} ground state of copper(II), confirmed by DFT, and is referred to as g_z in Table 2. Large differences between the remaining two g components indicate considerable energy difference between the excited copper orbitals d_{xz} and d_{yz}. The anisotropic exchange contribution to the D and E parameters is related to the exchange interactions in excited states represented by $J(z^2,n)$, in which one copper atom is in its ground state d_{z^2}, while the other is in the d_{xz} or d_{yz} excited state. The exchange interaction $J(z^2,xz)$ is expected to be stronger than $J(z^2,yz)$ because of spatial relations (X is parallel to Cu···Cu while Y is perpendicular), and as a result large E values are observed in all our complexes.

In conclusion, we have prepared and structurally characterized the first series of bimetallic copper(II) complexes that have a linear bridging X group (X = F^-, Cl^-, Br^-, OH^-). The antiferromagnetic coupling constant is very large in all cases, and the trend, measured here for *the first time*, is an increase along the series $F^- < Cl^- < OH^- < Br^-$, a trend supported by DFT calculations. EPR studies show that the systems have very anisotropic rhombic g tensors and large E parameters compared to D.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files in CIF format, description of the X-ray structural analysis, table of bond lengths and angles, experimental section, additional information related to the magnetic and EPR data, and results of the broken-symmetry DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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