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OPTIMIZATION OF FERROMAGNETIC COUPLING IN O/CO_2-BRIDGED COPPER(II) OLIGOMERS

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Abstract The ferromagnetic exchange coupling in the mixed-bridged system Cu(II)-O/CO_2-Cu(II) is investigated using SCF/CI calculations on dimeric model compounds. Starting from the geometry of the C_S-symmetric model molecule $[(H_2O)(CH_3O)Cu(\mu\text{-}O\text{-}CH_3O)(\mu\text{-}O,O'\text{-}HCO_2)Cu(H_2O)(CH_3O)]$, *M1*, with non-co-planar copper coordination planes, series of model molecules with varied geometries were developed and the singlet-triplet-splitting, $2J_{calc}$, calculated. The influences of following parameters were studied: the dihedral angle φ_{AB} between the copper coordination planes, $0° \leq \varphi_{AB} \leq 90°$, the copper-$\mu$-oxygen distance, 1.79 Å $\leq r_{Cu-O} \leq$ 2.09 Å, and the replacement of the H_2O ligands vs. NH_3 ligands. The optimized geometry for the strongest ferromagnetic coupling is expected for $\varphi_{AB} \sim 50 \pm 10°$, short Cu-O distances, and *O*-ligands instead of *N*-ligands. For planar geometries ($\varphi_{AB} \sim 0$) antiferromagnetic coupling is possible dependent on the Cu-O distance.

INTRODUCTION

A suggestion for the "construction" of molecular ferromagnets is based on high spin molecules or complexes and their magnetic coupling within the lattice.[1] As a first step the studies are concentrated on the nature of the high spin centres, especially on ferromagnetically exchange coupled metal centres. Their number is limited in comparison with the antiferromagnetically coupled oligomers. We found that the O/CO_2 mixed-bridged trimers $[Cu_3(R\text{-}C_6H_5CO_2)_4(R'_2NC_2H_4O)_2 L_n]$ are systems with quartet ground states due to a ferromagnetic

coupling in the Cu(II)-O/CO_2-Cu(II) subunit. Structural and magnetic properties of *1* (R = H; R' = C_2H_5; L = CH_3OH. n = 2) and *2* (R = H; R' = C_4H_9; L = C_2H_5OH. n = 2) were reported already.[2,3] Figure 1 presents the molecular structure of the 3-methyl derivative *3* studied recently.[4]

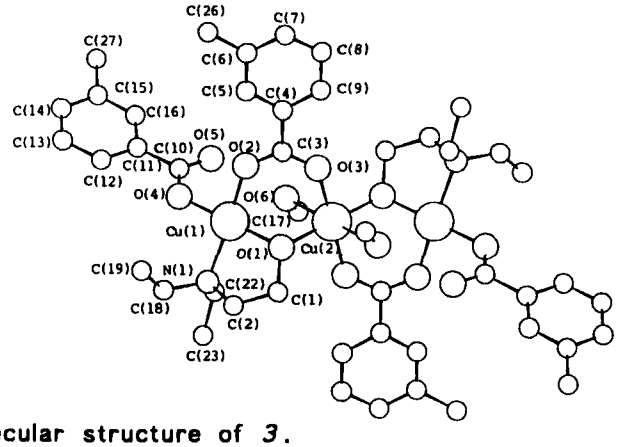

Figure 1. Molecular structure of *3*.

The structural investigations of *1* - *3* have shown, that the mixed-bridging leads to a "butterfly" geometry characterized by the dihedral angle φ_{AB} which is defined between the planes A [O(1), O(2), O(4), N(1)] and B [O(1), O(1)', O(3), O(3)']. For *1* - *3* nearly constant values of $\varphi_{AB} = 60 \pm 1°$ were found.

Therefore, we directed our interest towards the system Cu(II)-O/CO_2-Cu(II) to study the parameters for an optimized ferromagnetic coupling. A first, qualitative explanation for the quartet state in *1* - *3* was given on an AO-basis.[5] Now, the question arises which factors determine the strength of the coupling and if an antiferromagnetic ground state is possible also. Besides, it should be emphasized that the mixed-bridged dimeric skeleton is studied together with model complexes for the active site of the metallo protein hemocyanine.[6]

Our theoretical approach consists in calculation of $2J_{calc}$ in series of model complexes with various geometries. This procedure bases on an SCF/CI program developed by de Loth et al.[7] and was successfully applied for investigations of magneto-structural correlations in Cu_2O_2 systems,[8-10] also the ferromagnetic coupling in the heterobinuclear CuVO unit was verified on this way.[11]

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In this paper we summarize results of the theoretical calculation of the singlet-triplet-splitting, $2J_{calc}$, in Cu(II)-O/CO_2-Cu(II) systems. The conditions for the strongest ferromagnetic coupling in an optimized geometry are discussed. Further results and an AO-analyses of the magnetic orbitals will be presented in an extended report.[12]

MODEL COMPOUNDS, COMPUTATIONAL DETAILS

Model Molecule *M1*

The reason for the use of model compounds is given on one hand by the SCF/CI-procedure itself (limitation of basis set size, cpu time), on the other hand it is possible to study specificly the influence of geometric and electronic variations on $2J_{calc}$.

The C_s-symmetric model compound *M1* (Fig. 2) was derived from the geometry of *1*.[2] The coordinates in the x,y,z-system are listed in Table 1. The atoms O1, C1, C2, H1, and H3 (atom labels of real compounds were given with brackets, those of model compounds without brackets) are situated on the mirror plane (yz), the symmetry code * is -x, y, z. The dihedral angle φ_{AB} in *M1* is defined between the planes A [O1, O2, O3, O4] and B [O1, O2*, O3*, O4*].

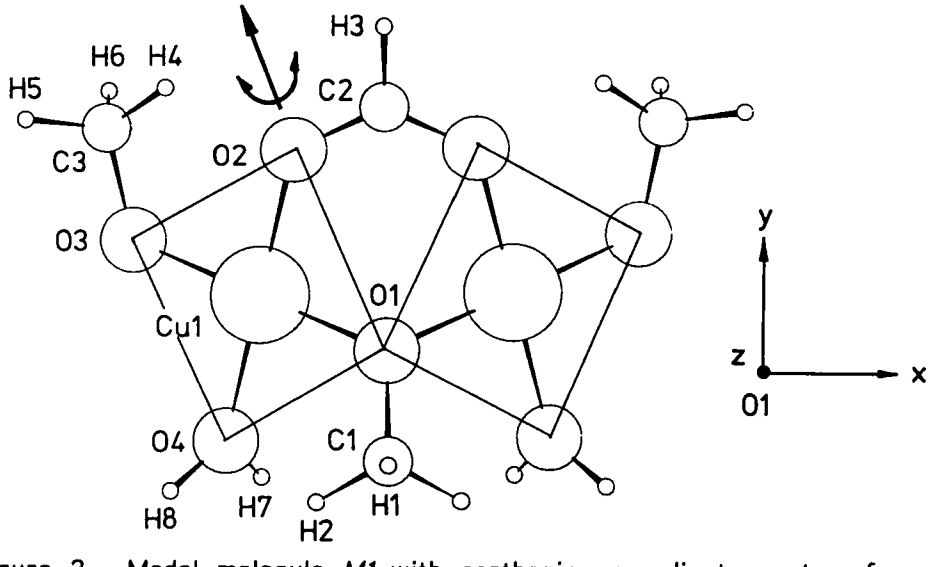

Figure 2. Model molecule *M1* with carthesian coordinate system for the SCF calculation.

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TABLE I Atomic coordinates for *M1* in the carthesian system [1 Å].

Atom	x	y	z
Cu1	-1.5353	0.7002	-0.9642
O1	0	0	0
O2	-1.1079	2.4857	-0.2120
O3	-3.0707	1.4003	-1.9284
O4	-1.9628	-1.0854	-1.7104
C1	0	-1.3605	0.4102
C2	0	3.0053	0
C3	-3.3830	2.7829	-1.8253
H1	0	-1.4118	1.4890
H2	-0.8817	-1.8526	0.0269
H3	0	3.9845	0.4557
H4	-2.6658	3.2673	-1.1792
H5	-4.3743	2.8986	-1.4127
H6	-3.3464	3.2348	-2.8055
H7	-1.5307	-1.5371	-2.4390
H8	-2.6486	-1.6934	-1.4246

Geometric and Electronic Variations

The *dihedral angle* φ_{AB} was varied in the range $0° \leq \varphi_{AB} \leq 90°$ by rotating the Cu1 coordination sphere (atoms Cu1, O3, O4, C3, H4 - H8; plane A, Fig. 2) around the O1-O2 vector in steps of 5°.

The variation of the *Cu1-O1 distance* (r_{Cu-O}) was performed by shifting the atoms Cu1, O3, O4, C3, H4 - H8 along the Cu1-O1 bond starting from the corresponding model with varied φ_{AB}. For r_{Cu-O} = 1.794, 2.094 Å model geometries over the whole φ_{AB}-range were calculated, at φ_{AB} = 0.7, 62.6° the variation of Cu1-O1 was divided in smaller steps.

The *influence of non-bridging ligands* was studied by replacing the H_2O ligands vs. NH_3 ligands (*O→N*; r_{Cu-O} = 1.944 Å). N1 was positioned on the Cu1-O4 bond with Cu1-N1 = 2.028 Å; for the hydrogen atoms tetrahedral arrangement was assumed (N1-H = 1.00 Å).

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Computational Details

The SCF-calculations were carried out with an extended version of the program PSHONDO.[13] Valence electrons were described by atomic orbitals, "core"-electrons by pseudopotentials. For Cu and O a double-ζ basis was used, N, C, and H atoms were represented by a minimal basis set, as reported previously.[8-10]

From the open-shell SCF-calculation two localized magnetic orbitals Φ_{Cu1} and Φ_{Cu1^*} were defined[7] using the singly occupied molecular orbitals σ_g and σ_u (Eq. 1). This procedure - originally applied to centrosymmetric molecules - can be transferred to C_s-symmetric Cu(II)-systems, as the irreducible representations of both point groups are described by the same matrix.

$$\Phi_{Cu1} = (\sigma_g + \sigma_u) / \sqrt{2} \qquad (1)$$
$$\Phi_{Cu1^*} = (\sigma_g - \sigma_u) / \sqrt{2}$$

The singlet-triplet-splitting, $2J_{calc}$, was obtained as a sum of different contributions arising from the following CI-treatment. This CI-procedure was described in previous reports[7-10] and should not be recalled here. The terms considered in these calculations were:

(1) Potential Exchange
(2) Kinetic Exchange
(3) Double Spin Polarization
(4) Charge Transfer Cu → Ligand
(5) Charge Transfer Ligand → Cu
(6) Kinetic Exchange - Polarization, 2nd order
(7) Kinetic Exchange - Polarization, 4th order

$$\Sigma = 2J_{calc}$$

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RESULTS AND DISCUSSION

Selected distances and angles in the model molecule *M1* are given in Table II. The copper-coordination sphere, CuO_4, is exactly planar and influences of tetrahedral distortions can be excluded. The dihedral angle φ_{AB} in *M1* is 71.3°.

TABLE II. Distances (Å) and angles (°) in *M1*. φ_{AB} is defined between the planes A [O1, O2, O3, O4] and B [O1, O2*, O3*, O4*].

Cu1-Cu1*	3.071	Cu1-O1-Cu1*	104.4
Cu1-O1	1.944	O1-Cu1-O2	88.1
Cu1-O2	1.982	O2-Cu1-O3	91.9
Cu1-O3	1.944	O3-Cu1-O4	88.1
Cu1-O4	1.982	O4-Cu1-O1	91.9
O2-C2	1.243	O1-Cu1-O3	180.0
		O2-Cu1-O4	180.0
		Cu1-O2-C2	129.4
φ_{AB}	71.3	O2-C2-O2*	126.1

The calculated spin coupling in the modelled molecules derived from *M1* are shown in Figure 3 as functions $2J_{calc}(\varphi_{AB}, r_{Cu-O})$ and $2J_{calc}(\varphi_{AB})$ for the *O→N* replacement, respectively.

Influence of the Dihedral Angle φ_{AB}

The variation of φ_{AB} is associated with changes in the bridging angle Cu1-O1-Cu1* and in the Cu1-Cu1* distance (Fig. 4). In the planar geometry ($\varphi_{AB} = 0°$, $r_{Cu-O} = 1.944$ Å) the metal centres are separated by 3.65 Å with an angle Cu1-O1-Cu1* = 141°. This aspect is interesting for the "biomimetic approach" as mentioned in the introduction. The folding up to a butterfly structure ($\varphi_{AB} = 90°$) decreases the Cu1-Cu1* distance to 2.75 Å and Cu1-O1-Cu1* to 90°. The model geometries are nearby the crystallographic values: In dimeric and trimeric structures φ_{AB} can vary between ~0° and 67° leading to the corresponding values for Cu1-Cu1* and Cu1-O1-Cu1*.[4,6,12]

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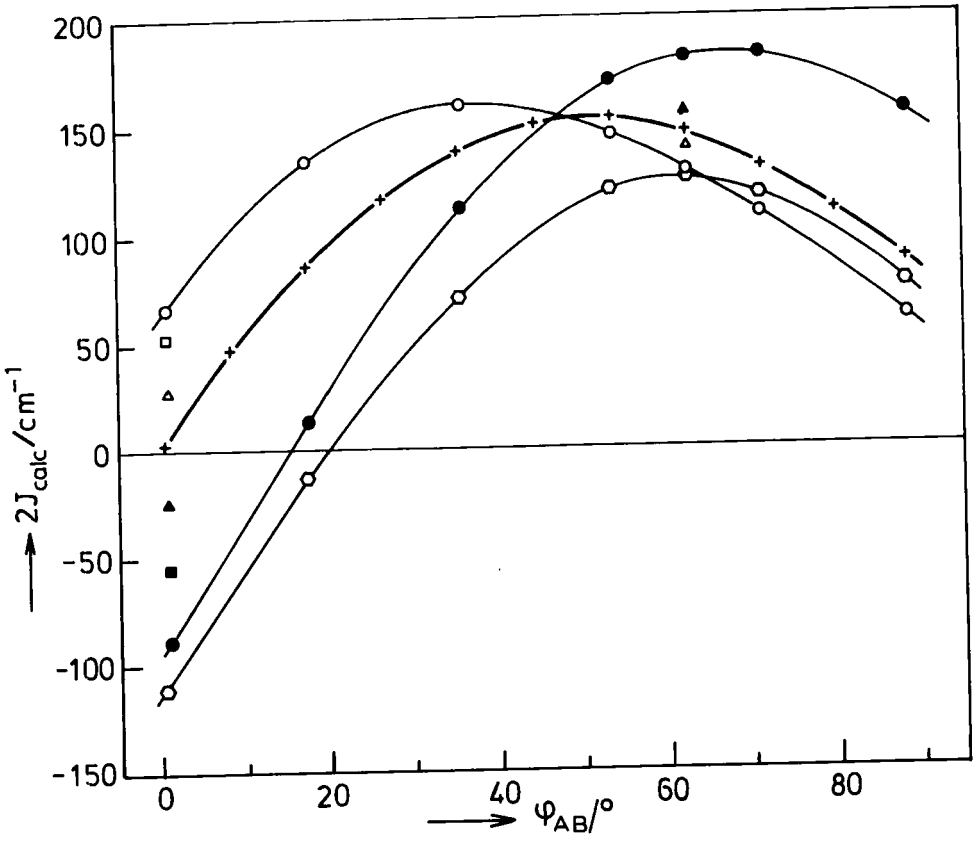

FIGURE 3. Calculated singlet-triplet-splittings, $2J_{calc}$, for model molecules of type *M1* as functions of the dihedral angle φ_{AB} with Cu1-O1 distances

r_{Cu-O} / Å = 1.794 (—●—); 1.994 (△)
1.844 (■), 2.044 (□)
1.894 (▲), 2.094 (—○—)
1.944 (—+—)

The replacement of *O* → *N* ligands is calculated with r_{Cu-O} = 1.944 Å (—⬡—).

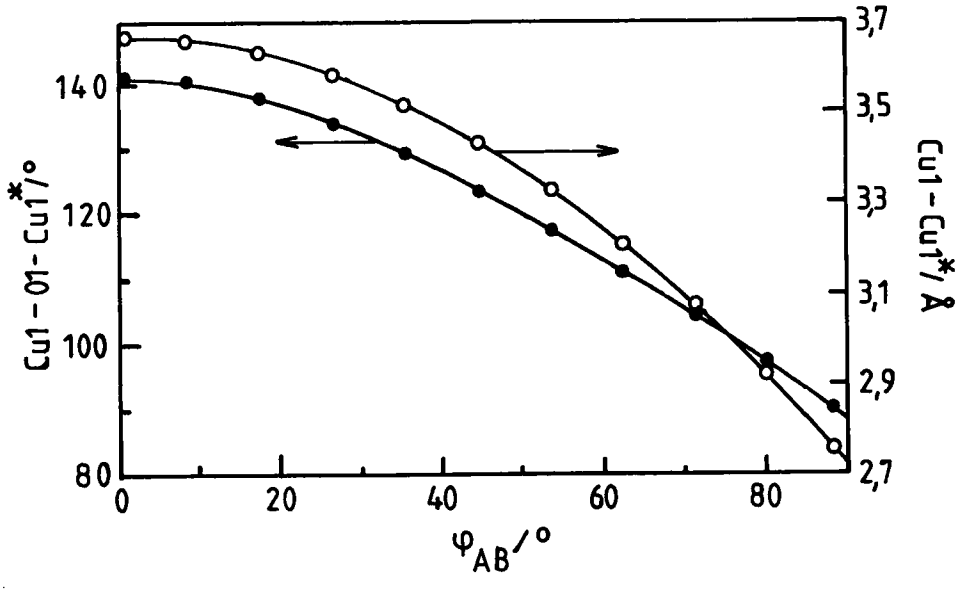

FIGURE 4. Variation of the Cu1-Cu1* distance and of the Cu1-O1-Cu1* angle with the dihedral angle φ_{AB} in dimeric model molecules of type *M1*, $r_{Cu-O} = 1.944$ Å.

These drastic geometric variations were not found for the magnetic behaviour: The function $2J_{calc}(\varphi_{AB}, r_{Cu-O} = 1.944$ Å) varies between 0 and 150 cm^{-1} with a parabolic shape (Fig. 3). For folded geometries the ferromagnetic coupling as found in compounds like *1* - *3* is confirmed by the model calculations. Towards the planar system $2J_{calc}$ decreases to zero. In comparison with the magneto-structural properties in Cu_2O_2-compounds[8-10] the mixed-bridged system investigated here is "invariable" against geometric changes and shows ferromagnetic coupling over a wide range.

The ferromagnetic coupling can be understood regarding the terms from the CI-treatment.[12] The dominant contributions are the ferromagnetic potential exchange, (1), and the antiferromagnetic kinetic exchange, (2), with $|(2)| < |(1)|$. Including the other contributions (3)-(7) the parabolic $2J(\varphi_{AB})$ functions are obtained. An analyses of the atomic orbitals involved in the singly occupied molecular orbitals σ_g and σ_u will be reported elsewhere.[12]

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Influence of the Cu1-O1 Bond Length

At shorter Cu1-O1 bond lengths (r_{Cu-O}) a more distinct $2J(\varphi_{AB})$ is obtained: For $\varphi_{AB} \to 0°$ weak antiferromagnetic coupling results which changes into ferromagnetic coupling with increasing φ_{AB}. Geometries with long Cu1-O1 distances show an overall ferromagnetic behaviour.

The r_{Cu-O} influence depends on the degree of folding: Planar systems tend towards antiferromagnetic coupling with decreasing r_{Cu-O}, folded systems towards a stronger ferromagnetic coupling. In consequence of that no influence of r_{Cu-O} is observed around $\varphi_{AB} \approx 47°$.

A comparable behaviour is reported for the Cu_2O_2-systems. For bridging angles Cu-O-Cu' around 93° the calculated singlet-triplet-separations don't depend on the Cu-O distance.[9]

Replacement of *O*- vs. *N*-Ligands

In Figure 3 this effect of non-bridging ligands is compared for $r_{Cu-O} =$ 1.944 Å. *N*-ligands favour an antiferromagnetic coupling, especially for $\varphi_{AB} \to 0°$. With increasing φ_{AB} both functions get closer, and at $\varphi_{AB} \to 90°$ nearly no difference between *N*- and *O*-coordination is obtained. The reduced ferromagnetic coupling might be a consequence of the smaller electronegativity of nitrogen in comparison with oxygen.

Comparable results were obtained for the Cu_2O_2-system within the serie of Br. Cl. F as non-bridging ligands.[9]

Optimized Conditions for the Ferromagnetic Coupling

These calculations can be used to deduce the conditions for an optimized ferromagnetic coupling in the Cu(II)-O/CO_2-Cu(II) system. They can be summarized as

- Folded geometry ("butterfly-structure"), $40 < \varphi_{AB} < 60°$
- Short Cu1-O1 distances
- Non-bridging *O*-ligands instead of *N*-ligands.

Another result should be emphasized: This mixed-bridged system is a socalled "Invariable System" in the region $\varphi_{AB} > 40°$ which is only slightly influenced by geometric and electronic variations. Small changes in geometry don't affect on the ferromagnetic coupling. Therefore compounds like *1* - *3* with O/CO_2-bridging might be suitable to built up molecular ferromagnets.

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Extended version including 160 contracted Gaussian orbitals, 300 Gaussian primitives by H. Astheimer, L. Walz, and J.-P. Daudey.

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