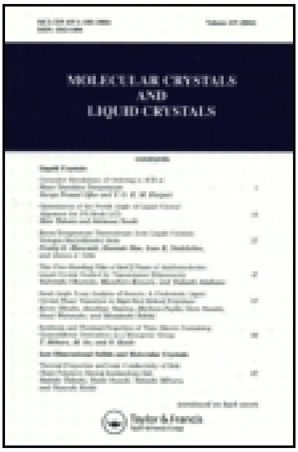

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Magneto-Structural Correlations in Dimeric Copper(II) Carboxylates

Shigeru Ohba [a] , Michinobu Kato [b] , Tadashi Tokii [c] , Yoneichiro Muto [d] & Omar W. Steward [e]

[a] Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, Kohoku-ku, Yokohama, 223, Japan

[b] 13-30, Takatorikita 4, Asaminami-ku, Hiroshima, 731-01, Japan

[c] Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga, 840, Japan

[d] 13-3, Mizugae-cho 2, Saga, 840, Japan

[e] Department of Chemistry, Duquesne University, Pittsburgh, PA, 15282, U.S.A.

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SHIGERU OHBA
Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3, Kohoku-ku, Yokohama 223, Japan

MICHINOBU KATO
13–30, Takatorikita 4, Asaminami-ku, Hiroshima, 731–01, Japan

TADASHI TOKII
Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840, Japan

YONEICHIRO MUTO
13–3, Mizugae-cho 2, Saga 840, Japan

and OMAR W. STEWARD
Department of Chemistry, Duquesne University, Pittsburgh, PA 15282, U.S.A.

Abstract For dimeric copper(II) carboxylates, the most important factor determining the strength of the spin superexchange interactions is the electronic structure of the carboxylato bridge. It also has been revealed that the trigonal bipyramidal deformation of the coordination geometry around the copper atoms, and the bending of the carboxylato bridge decrease the antiferromagnetic interactions.

INTRODUCTION

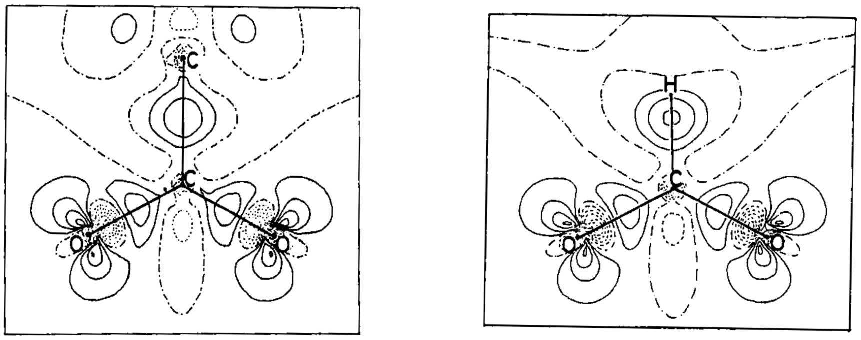
Dimeric copper(II) carboxylates which contain four bridging carboxylato ligands have antiferromagnetic properties with a singlet ground state. In these systems, the spin superexchange pathway plays an important role, *i.e.*, their magnetic properties are associated with the coupling of the unpaired electrons of the Cu(II) atoms through the bridging ligands.[1,2] The magnitude of the magnetic exchange interaction can be estimated by the singlet-triplet energy separation, $-2J$. The $-2J$ values of the dimeric copper(II) carboxylates have been observed to be *ca.* 300, 500, and 1000 cm^{-1} for the copper(II) acetate, formate, and triorganosilanecarboxylate dimers, respectively. Furthermore, the dimeric copper(II) trichloroacetate complexes themselves show a variation of $-2J$ from 74 to 240 cm^{-1}.[3] We have sought the origin of the variation of $-2J$. The results of our several investigations are summarized.

ELECTRONIC STRUCTURE OF THE CARBOXYLATO BRIDGE

Copper(II) Formates, Acetates, and Silanecarboxylates

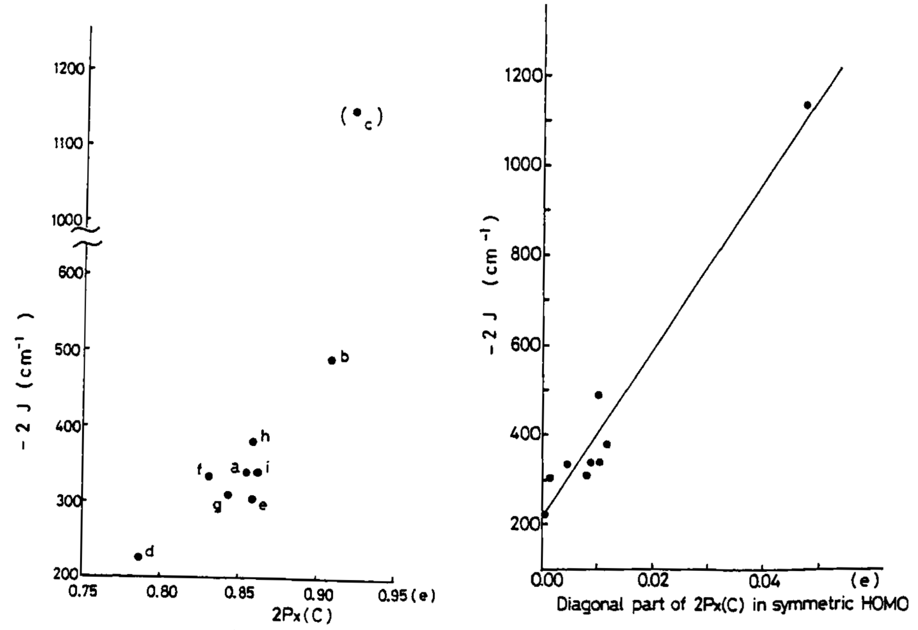
The molecular structures of copper(II) formates and acetates with pyridine and urea ligands were compared precisely.[4] The structures of the dimeric copper(II) formates and acetates with 2-, 3-, or 4-picoline as the axial ligand were compared in order to confirm that no important geometrical differences occur in the cage structure.[5] The structures of the copper(II) triorganosilanecarboxylate and -germanecarboxylate dimers were determined by X-ray diffraction and found to be of the copper(II) acetate monohydrate type having a square-pyramidal coordination geometry around the Cu atoms.[6] There exist no special features in the dimensions of the $[Cu_2(RCOO)_4]$ cage of the silane- or germanecarboxylates which can account for their very strong spin superexchange interactions. Thus we were encouraged to seek other properties of the system with which to correlate the $-2J$ value.

The chemical bond in a molecule can be analysed by the deformation density, which is the difference between the electron density of the molecule and the electron densities of the neutral spherical atoms in the ground states. The deformation densities for the formate and acetate ions were calculated by an *ab initio* SCF method, using a MIDI4* (double-zeta + polarization function) basis set.[5] As seen in Figure 1, the deformation densities of the COO^- moiety in the acetate and formate ions are nearly identical, as one would expect from the transferability of charge densities in small fragments.[7] The C-O bonding and the O atom lone-pair peaks are consistent with sp^2 hybridization of the C and O atoms. Mulliken population analyses for the $RCOO^-$ ions (R=CH_3, H, $SiMe_3$, CCl_3, $CHCl_2$, CH_2Cl, CF_3, CHF_2, CH_2F, CMe_3 and CH_2CH_3) also were carried out using an STO-6G (minimal) basis set. The effective charges on the C and O atoms of the COO^- moiety are +0.233, -0.529 for R=CH_3, +0.164, -0.531 for R=H, and +0.072, -0.499 *e* for R=$SiMe_3$, respectively. The net charges on the central C atoms differ slightly from each other. The key factor is the $2p_x$ orbital population (taking the x axis parallel to the C-R bond); the values are 0.855, 0.908, and 0.922 for R=CH_3, H and $SiMe_3$, respectively. These results indicate that the greater the electron density on the carboxylate C atom, the stronger the antiferromagnetic interaction in the binuclear copper(II) carboxylate (see Figure 2a). This is in accord with the tendency of the spin-exchange interaction to increase as the carboxylate substituent becomes a stronger electron donor.[8,9] Although relating the magnetic properties of dimeric copper(II) carboxylates based on the charge distributions in the isolated carboxylato ligands involves some assumptions, a qualitative analysis seems appropriate.



(a) (b)

FIGURE 1 Theoretical deformation densities for (a) CH_3COO^- and (b) $HCOO^-$ ions. The contour interval is 0.2 $e\ \AA^{-3}$. The negative contours are dotted, the zero contours chain-dotted.



(a) (b)

FIGURE 2 The average $-2J$ value of $[Cu(RCOO)_2\ L]_2$ *versus* (a) the $2p_x$ electron population of the central C atom and (b) the diagonal part of $2p_x(C)$ in the symmetric HOMO. (a)-(i) stand for R=CH_3, H, $SiMe_3$, CCl_3, $CHCl_2$, CH_2Cl, CF_3, CH_2CH_3, CMe_3, respectively.

Correlation Between $-2J$ and the Electron Population

The $-2J$ values of the corresponding dimeric copper(II) carboxylates with a square-pyramidal coordination geometry around copper were selected, and the averages were calculated. Figure 2(b) shows a correlation of $-2J$ with the diagonal part of the $2p_x$ electron population of the central C atom in the symmetric HOMO, *i.e.*, twice the square of the coefficient of the $2p_x$ atomic orbital. Essentially this observation is in accordance with the spin-exchange mechanism proposed by Hay, Thibeault and Hoffmann.[2] In this mechanism, the symmetric metal MO overlaps with the symmetric highest occupied MO's (HOMO's) of the bridging carboxylate ions (see Figure 3a). The symmetric HOMO of the carboxylate ion is constructed predominantly from the $2p_x$ orbitals of the O atoms and from the $2s$ and $2p_x$ orbitals of the central C atom. The polar character of R in $RCOO^-$ is transmitted primarily to the $2p_x$ orbital of the C atom. Even though the coefficient of the $2p_x$ (C) orbital is small in the symmetric HOMO, magnetic orbital overlaps can be constructed such as $2p_x$(O)-$2p_x$ (C)-$2p_x$(O), which overlap with the symmetric metal MO.[10] This appears to explain why only the electron population of the $2p_x$(C) orbital correlates strongly with the spin-exchange interactions. Clearly, the very large $-2J$ values observed for the copper(II) triorganosilanecarboxylates originate from the special electronic structure of the central C atom. On the other hand, the asymmetric HOMO of the carboxylate ion is predominantly constructed from the $2p_x$ and $2p_y$ orbitals of the O atoms and with the $2p_y$ orbital of the C atom (y lies along the O$\cdots$O direction). The coefficient of the $2p_y$(C) atomic orbital varies from 0.064 to 0.077, showing almost no modification by the polar effect of the substituent group. Thus, the electronic structure of the central C atom is the primary factor determining the strength of the spin superexchange interaction. A secondary factor may be the Cu-O bond strength, which can be estimated by the effective charge of the O atom or assessed roughly from the pK_a of the carboxylic acid. However, it does not seem to be explicitly reflected in the Cu-O bond length. The atom X bonded to the COO^- ion is limited to C, H, and Si in the above study. When X=Ge, the $-2J$ value of the complex is similar to that of the corresponding silanecarboxylato complex.[6] The very weak antiferromagnetic interaction of the carbamato complex, where X=N, is attributed to the small coefficient of the $2p_x$(C) in the symmetric HOMO.[5]

BENDING OF THE CARBOXYLATO BRIDGE

Copper(II) Benzoates

The quinoline adduct of dimeric copper(II) benzoate has a smaller $-2J$ value (267 cm^{-1}) than the other copper(II) benzoate adducts, for example, the pyridine adduct,

$-2J = 328$ cm^{-1}. There are no abnormal bond lengths or bond angles in the quinoline adduct.[11] The possiblity of an accidental inconsistency between the crystal structure and the $-2J$ value caused by polymorphism or a phase transition was ruled out. The abnormal $-2J$ value of [Cu(PhCOO)$_2$ quinoline]$_2$ was confirmed several times by magnetic susceptibility measurements. Therefore, we determined the crystal structures and $-2J$ values of several copper(II) benzoates with substituted quinoline ligands (4-Me-quinoline, 7-Me-quinoline, and 4,7-Cl$_2$-quinoline) and other axial ligands (PhCOOH, 3-picoline, caffeine) in order to solve the conundrum as to why the quinoline adduct has such an abnormally small $-2J$ value.[12]

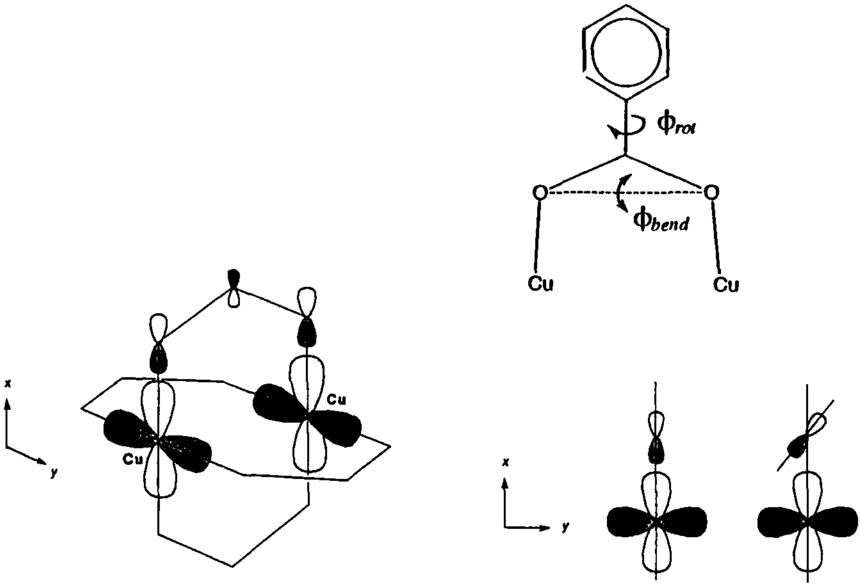
The complexes with the substituted quinoline ligands show normal $-2J$ values, 321-337 cm^{-1}. The abnormally small $-2J$ value of the quinoline adduct, 267 cm^{-1} , cannot be attributable to the small differences in bond lengths or the bond angles of the [Cu$_2$(COO)$_4$] cage. The coordination geometry around the Cu atoms is square pyramidal for all the complexes including the quinoline adduct, and there is no tendency towards trigonal bipyramidal deformation. The imbalance in the Cu—N—C angles involving the axial ligand resulting from intramolecular repulsions is observed not only for the quinoline adduct, but also for the substituted quinoline and caffeine adducts.

The molecular structure was projected along the Cu···Cu axis in order to find the structural specificity of the quinoline adduct. The rotation angles of the Ph group relative to the COO moiety in the bridging benzoate ions, ϕ_{rot}, and the bending angles of the OCO moiety relative to the Cu—O···O—Cu plane, ϕ_{bend}, are found to be larger in the quinoline adduct than the other adducts. These deformations of the molecular structure are the result of packing effects. For an isolated binuclear complex, the symmetric structure with $\phi_{\text{rot}} = \phi_{\text{bend}} = 0°$ is expected to have the least strain energy. However, the molecular structure may be deformed in the crystals so as to improve the packing efficiency, where the increased intramolecular strain energy is compensated by the reduced intermolecular interactions. The reason that only the quinoline adduct of the copper(II) benzoate complexes is so deformed in the crystal, is not clear at present.

Decrease of $-2J$ by Bending of the Bridge

An *ab initio* molecular orbital calculation suggests that the electronic structure of the PhCOO$^-$ ion is not altered drastically by increasing the rotation angle, ϕ_{rot} from 0 to 90°.[12] In fact, the 2-substituted benzoate complex, [Cu(2-Me-PhCOO)$_2$ py]$_2$ shows a normal $-2J$ value of 340 cm^{-1}, although the mean ϕ_{rot} angle is 34.4(6)°. Therefore, the abnormally small $-2J$ value for crystalline [Cu(PhCOO)$_2$ quinoline]$_2$ cannot be attributed to the ϕ_{rot} angle of 19.5(8)°. From the above considerations, the small

$-2J$ value of the quinoline adduct is the result of the bending angle of the bridge, ϕ_{bend}. As illustrated in Figure 3(a), the unpaired electrons in the $d_{x^2-y^2}$ orbital of the Cu(II) atoms interact with each other through the molecular orbitals of the bridging ligands. The spin super-exchange interaction of the binuclear Cu(II) complexes can be understood in terms of the natural (non-orthogonalized) magnetic orbitals.[13] The natural magnetic orbital (NMO) of the Cu atom in the cage structure is mainly the $d_{x^2-y^2}$ orbital which has tails on the bridges. The spin super-exchange interaction increases along with increase of the overlap integral of the two NMO's. When the Cu—O—C—O—Cu bridge bends, the overlap between the $d_{x^2-y^2}$ orbital of the Cu(II) atoms and the $2p_x$ orbital of the benzoate oxygen atoms in the symmetric HOMO decreases, and the tails of the NMO on the bridge decrease. Consequently, the spin super-exchange interaction in the quinoline adduct is suppressed by the smaller overlap of the NMO's in the bent bridges compared to the coplanar bridges. The abnormally small $-2J$ value (262 cm^{-1}) of $[\text{Cu(2-Cl-PhCOO)}_2\ \text{H}_2\text{O}]_2$ is also attributed to the bending of one of the bridges, $\phi_{\text{bend}}=2.2(1)$ and $12.5(1)°$. [14]



(a) (b)

FIGURE 3 Schematic drawing of the overlap between the $d_{x^2-y^2}$ orbitals of the Cu(II) atoms and the symmetric HOMO of the bridging carboxylate ion: (a) a perspective view and (b) partial projections of the normal and bent bridges along the Cu···Cu axis.

DEFORMATION OF THE COORDINATION GEOMETRY

Copper(II) Trichloroacetates

Crystal structures of dimeric copper(II) trichloroacetates have been determined by single-crystal X-ray diffraction.[15] The Cu···Cu distances, O-Cu-O angles and the $-2J$ values are listed in Table I. In the crystals of the compounds which have a small -2J values, less than *ca.* 200 cm^{-1}, the coordination geometry around the Cu atom is deformed from square-pyramidal (SP) toward trigonal-bipyramidal (TBP). Deformation of the cage is specified by several geometrical parameters: (a) the Cu···Cu distance, (b) the average deviation of the Cu—O—C bond angles from 123°, (c) the summation of the bond distances in the Cu—O—C—O—Cu bridge, and (d) the longest Cu—O bond distance. Linear correlations were observed between the -2J values and these geometrical parameters (see Figure 4).

Among the large number of dimeric copper(II) carboxylates studied so far, the TBP structure has only been observed for copper(II) trichloroacetates and triphenylacetates, $[Cu(Ph_3CCOO)_2\ py]_2$.benzene ($-2J = 187\ cm^{-1}$).[16] The stronger acidity of trichloroacetic acid (pK_a=0.7 in aqueous solution) than acetic acid (pK_a=4.75) suggests that the Cu-O bond is weaker and the cage structure more flexible for the trichloroacetate ion than for the corresponding acetate complexes.[17] The energy difference between the SP and the TBP molecular structures may be of the same order of magnitude as that of the intermolecular interactions in the crystals. As a consequence, the cage structure may be deformed by the crystal packing forces. In fact, certain copper(II) trichloroacetate dimers crystallize in several packing modes when different solvents of crystallization are used and yield complexes with a variety of $-2J$ values. For example, the caffeine adduct forms the TBP structure in $[Cu(Cl_3CCOO)_2$ caffeine$]_2$ ($-2J$=136 cm^{-1}) on crystallization from chloroform, and the SP structure in $[Cu(Cl_3CCOO)_2$ caffeine$]_2$.2benzene ($-2J$=203 cm^{-1}) from benzene.[18] The driving force for the TBP deformation of the copper(II) triphenylacetate dimer may be the intermolecular non-bonded repulsions of the bulky triphenylmethyl groups. Also it is revealed that the TBP deformation is caused by the bulky monodentate ligand, 2,6-lutidine, in crystals of $[Cu(PhMe_2CCOO)_2$ 2,6-lutidine$]_2$.benzene.[21]

Decrease of -2J by the TBP Deformation

The magneto-structural data indicate that the spin super-exchange interaction in dimeric copper(II) system is weaker in the TBP than in the SP structure. The spin-exchange interaction in these systems can be described using the concept of magnetic orbitals.[13] The small $-2J$ values for the TBP structure are related to the magnetic orbitals of the complexes (see Figure 5). Using a simple model, the spin densities of the Cu(II) atoms are localized in the $d_{x^2-y^2}$ orbitals in the SP structure, and

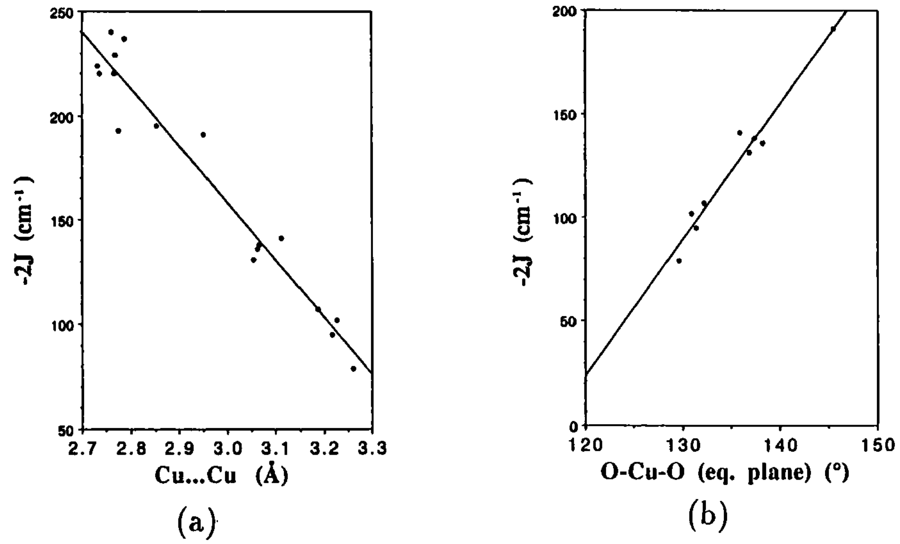


FIGURE 4 Linear correlations between the $-2J$ values of the dimeric copper(II) trichloroacetates and (a) the Cu···Cu distances, and (b) the equatorial O—Cu—O bond angles of the TBP structure. The squares of the correlation coefficient are (a)0.949 and (b)0.960.

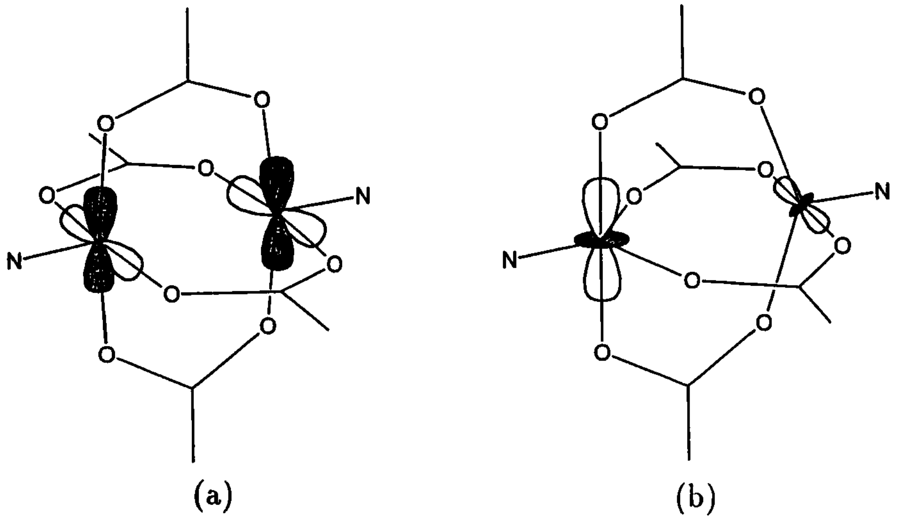


FIGURE 5 Schematic drawing of the magnetic orbitals in (a) the SP, and (b) the TBP structures.

TABLE I Comparison of the Cu···Cu distances(Å) of the copper(II) trichloroacetates and their $-2J(\text{cm}^{-1})$ values

Compound	Cu···Cu	Type [a]	O-Cu-O_{eq} [b]	$-2J$	Ref.
$[Cu(Cl_3CCOO)_2$ 2-Et-py$]_2$	3.261(1)	TBP	129.6(1)	79	(15)
$[Cu(Cl_3CCOO)_2$ 2,3-Me_2-py$]_2$.Toluene	3.216(2)	TBP	131.5(3)	95	(15)
$[Cu(Cl_3CCOO)_2$ 2,5-Me_2-py$]_2$.Toluene	3.226(1)	TBP	131.0(2)	102	(15)
$[Cu(Cl_3CCOO)_2$ 3,4-Me_2-py$]_2$	3.186(2)	TBP	132.3(2)	107	(15)
$[Cu(Cl_3CCOO)_2$ 2-Cl, 5-NO_2-py$]_2$	3.054(3)	TBP	136.9(4)	131	(15)
$[Cu(Cl_3CCOO)_2$ caffeine$]_2$	3.062(1)	TBP	138.2(1)	136	(15)
$[Cu(Cl_3CCOO)_2$ 3-CN-py$]_2$	3.066(1)	TBP	137.4(2)	138	(15)
$[Cu(Cl_3CCOO)_2$ 2,5-Cl_2-py$]_2$.Benzene	3.113(3)	TBP	135.9(4)	141	(15)
$[Cu(Cl_3CCOO)_2$ 2,5-Cl_2-py$]_2$	2.951(1)	TBP	145.5(2)	191	(15)
$[Cu(Cl_3CCOO)_2$ 3-Cl-py$]_2$	2.774(1)	SP		193	(15)
$[Cu(Cl_3CCOO)_2$ caffeine$]_2$.2Benzene	2.852(2)	SP		195	(18)
$[Cu(Cl_3CCOO)_2$ 2-Cl-py$]_2$	2.766(3)	SP		220	(19)
$Cu_2(Cl_3CCOO)_4$(caffeine).2Toluene	2.736(1)	SP		220	(15)
$[Cu(Cl_3CCOO)_2$ Ph-CN$]_2$	2.732(1)	SP		224	(20)
$[Cu(Cl_3CCOO)_2$ 4-CN-py$]_2$	2.769(1)	SP		229	(15)
$[Cu(Cl_3CCOO)_2$ 4,7-Cl_2-quinoline$]_2$	2.786(1)	SP		237	(15)
$[Cu(Cl_3CCOO)_2$ 2-F-btz$]_2$ [c]	2.761(3)	SP		240	(15)

a. TBP structure has axial O-Cu-O bond angles greater than 173°.

b. The mean value of the equatorial O-Cu-O bond angles(°) of the TBP structure.

c. btz = benzothiazol.

the magnetic orbitals effectively overlap with each other through the four bridging carboxylato ligands. However, in an ideal TBP structure, the magnetic orbitals consist mainly of d_{z^2} orbitals, which are perpendicular to each other at the two Cu(II) sites. These magnetic orbitals overlap only slightly with each other through the orbitals of the bridging groups. Therefore, the spin super-exchange interactions are suppressed by the TBP deformation. The extent of the distortion toward TBP can be characterized by the O—Cu—O bond angle between the opposite bridges; this angle is larger than 173.4(2)° for TBP structure in the axial directions and smaller than 166.7(2)° for SP structures. A good correlation is observed between the -2J values and the equatorial O—Cu—O bond angles of the TBP complexes as shown in Figure 4(b), indicating that the TBP structure with the O-Cu-O angle of 120 ° may have a -2J value of *ca* 25 cm^{-1}.

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