Exchange Coupling in Symmetrically *syn,syn*-Mono(carboxylato)-Bridged Dinuclear Copper(II) Complexes

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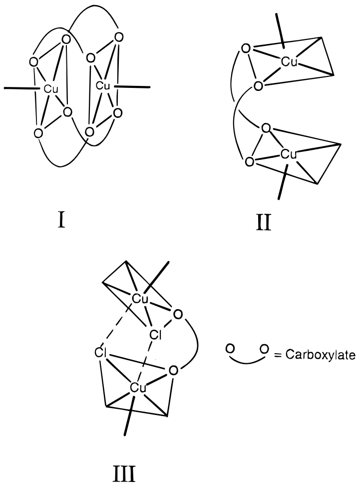
Introduction

Dinuclear tetrakis(μ-carboxylato)-bridged complexes [Cu^{II}_2(μ-carboxylato)$_4$$X_2$] where X represents H_2O, pyridine, urea, or an O-bound carboxylic acid represent the archetype species for intramolecular antiferromagnetic exchange coupling between two paramagnetic metal ions (Chart 1).[1,2] The strength of this exchange coupling is measured by the coupling constant *J* within the usual isotopic Heisenberg−Dirac−van Vleck (HDvV) model ($H = -2JS_1S_2$; $S_1 = S_2 = {}^1/_2$) where 2*J* represents the singlet−triplet energy gap. For complexes of the above type, very strong intramolecular antiferromagnetic coupling has been observed in the range −160 to −350 cm^{-1} for J^{1-3} depending on the nature of the carboxylic acid and the apical ligands. The mechanism of this interaction has been demonstrated to be a superexchange of magnetic $d_{x^2-y^2}$ orbitals through the bridging acetates.[4]

Recently a few dinuclear complexes [$L^1_2Cu^{II}_2(\mu\text{-}O_2CR)_2(H_2O)_2]^{2+}$ were synthesized and structurally characterized.[5] These compounds contain only *two* symmetric *syn*,*syn*-carboxylato bridges (Chart 1), and L^1 represents a didentate ligand (1,10-phenanthrolin, 2,2′-bipyridine). Interestingly, the exchange coupling between the two $d_{x^2-y^2}$ magnetic orbitals is still antiferromagnetic, yielding an $S = 0$ ground state, but significantly weaker ($J = -43$ to -63 cm^{-1}) than in the above tetrakis(μ-carboxylato)dicopper(II) series. Tokii et al.[5a] have ascribed this diminished coupling predominantly to the fact that the latter complexes contain only two bridging carboxylates in contrast to four in the above series. In order to further investigate the validity of this implied magneto−structural correlation between the number of bridges and the strength of the magnetic exchange, we prepared the dinuclear copper complex [{$LCu^{II}Cl$}$_2$(μ-benzoato)](ClO_4), **1**, and its bromo analogue [{$LCu^{II}Br$}$_2$(μ-benzoato)](ClO_4), **2** (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), which contain *one* bridging *syn*,*syn*-benzoate. Here we report the synthesis, crystal structure, and magnetic properties of these two compounds and the exchange coupling constants determined from the temperature-dependent magnetic susceptibility data.

Chart 1



Experimental Section

Caution! Although we have not encountered any problems, it is noted that perchlorate salts are potentially explosive and should be handled in small quantities only with appropriate care.

The ligand 1,4,7-trimethyl-1,4,7-triazacyclononane (L) was prepared according to published procedures.[6]

[{$LCu^{II}Cl$}$_2$(μ-benzoato)](ClO_4), 1. To a solution of $CuCl_2 \cdot 2H_2O$ (180 mg; 1.2 mmol) in methanol (30 mL) was added a methanolic solution (10 mL) of benzoic acid (140 mg; 1.1 mmol) containing 4 drops of piperazine. To the resulting deep green solution was added with stirring at room temperature a 1.0 M methanolic solution of L (1 mL). Addition of $NaClO_4$ (300 mg) initiated the precipitation of green microcrystals. Single crystals suitable for X-ray crystallography grew from the resulting solution overnight. The yield was 0.53 g (58%). Anal. Calcd (found) for $C_{25}H_{47}Cl_3Cu_2N_6O_6$: C, 39.45 (39.2); H, 6.22 (6.1); N, 11.04 (11.0). UV−vis (CH_3CN): 228 nm ($\epsilon = 12.6 \times 10^3$ L mol^{-1} cm^{-1}), 284 (12.5×10^3), 380 (710), 707 (78), 1177 (22).

[{$LCu^{II}Br$}$_2$(μ-benzoato)](ClO_4) 2. This complex was prepared as described above for **1** by using $CuBr_2$ as starting material. The yield was 0.63 g (67%). Anal. Calcd (found) for $C_{25}H_{47}Br_2Cu_2N_6O_6$: C, 35.32 (34.9); H, 5.53 (5.5); N, 9.89 (9.8). UV−vis (CH_3CN): 230 nm (ϵ 13.1×10^3 L mol^{-1} cm^{-1}), 282 (11.1×10^3), 684 (138), 1159 (53).

X-ray Crystallography. Intensities and lattice parameters of a green needle-shaped crystal of **1** were measured at 293 K on a Siemens P4 diffractometer by using monochromated Mo Kα radiation. Crystal parameters and details of the data collection and refinement are summarized in Table 1 (for full details see the Supporting Information). Correction for absorption effects was carried out (ψ scans). The structure was solved by direct methods; the Siemens program package SHELXTL-PLUS (PC version)[7] was used throughout. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F) + 0.0002F^2$.

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(1) (a) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, A* **1952**, *214*, 451. (b) Kato, M.; Muto, Y. *Coord. Chem. Rev.* **1988**, *92*, 45. (c) Doedens, R. J. *Prog. Inorg. Chem.* **1976**, *21*, 209.

(2) Recent crystal structure determinations: (a) Uekusa, H.; Ohba, S.; Saito, Y.; Kato, M.; Tokii, T.; Muto, Y. *Acta Crystallogr.* **1989**, *C45*, 377. (b) Yamanaka, M.; Uekasa, H.; Ohba, S.; Saito, Y.; Iwata, S.; Kato, M.; Tokii, T.; Muto, Y.; Steward, O. W. *Acta Crystallogr.* **1991**, *B47*, 344. (c) Kanata, T.; Uekasa, H.; Ohba, S.; Furukawa, T.; Tokii, T.; Muto, Y.; Kato, M. *Acta Crystallogr.* **1992**, *B48*, 253. (d) Usubaliev, B. T.; Movsumov, E. M.; Musaev, F. N.; Nadzafov, G. N.; Amiraslanov, I. R.; Mamedov, H. S. *Koord. Khim.* **1980**, *6*, 1091. (e) Barclay, G. A.; Kennard, C. H. L. *J. Chem. Soc.* **1961**, 5244.

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(6) Wieghardt, K.; Chaudhuri, P.; Nuber, B.; Weiss, J. *Inorg. Chem.* **1982**, *21*, 3086.

(7) Full-matrix least-squares structure refinement program package SHELXTL-PLUS: G. M. Sheldrick, Universität Göttingen.

0020-1669/96/1335-2704$12.00/0

Table 1. Crystallographic Data for **1**

formula	$C_{25}H_{47}Cl_3Cu_2N_6O_6$	V, Å^3	6711(2)
fw	761.1	Z	8
cryst syst	orthorhombic	T, °C	22
space group	*Pbca*	ρ_{calcd}, g cm^{-3}	1.507
a, Å	14.175(3)	μ, mm^{-1}	1.553
b, Å	18.768(4)	R^a	0.055
c, Å	25.225(5)	$R_w{}^a$	0.051

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for the Cation in Crystals of **1**

	x	y	z	U(eq)^a
Cu1	376(1)	1975(1)	777(1)	35(1)
Cu2	2357(1)	1310(1)	1493(1)	35(1)
Cl1	460(1)	900(1)	1234(1)	50(1)
Cl2	2405(1)	1939(1)	699(1)	49(1)
O1	1835(3)	2135(2)	1872(2)	41(2)
O2	563(3)	2544(2)	1434(2)	41(2)
N1	343(4)	2926(2)	325(2)	39(2)
N2	−1215(3)	2165(3)	783(2)	45(2)
N3	60(4)	1494(3)	53(2)	41(2)
N4	3007(4)	410(3)	1193(2)	51(2)
N5	2304(4)	718(3)	2203(2)	42(2)
N6	3857(4)	1539(3)	1792(2)	50(2)
C1	−645(5)	3217(4)	297(3)	49(3)
C2	−1271(5)	2947(4)	727(3)	52(3)
C3	−1602(5)	1774(4)	325(3)	52(3)
C4	−921(5)	1213(4)	130(3)	53(3)
C5	100(5)	2031(4)	−377(3)	54(3)
C6	667(5)	2674(4)	−201(3)	51(3)
C7	992(5)	3485(4)	514(3)	57(3)
C8	−1658(5)	1938(5)	1278(3)	62(3)
C9	695(5)	892(4)	−87(3)	58(3)
C10	2915(7)	−172(5)	1582(4)	90(4)
C11	2287(6)	−35(4)	2010(3)	69(3)
C12	3154(6)	849(5)	2523(3)	76(4)
C13	3747(6)	1423(6)	2366(3)	76(4)
C14	4456(5)	1009(6)	1536(4)	85(4)
C15	4006(6)	604(6)	1110(3)	83(4)
C16	2622(6)	169(5)	670(3)	68(3)
C17	1445(5)	853(4)	2519(3)	58(3)
C18	4176(6)	2260(5)	1683(4)	85(4)
C19	1140(4)	2542(4)	1810(3)	33(2)
C20	996(5)	3106(4)	2231(3)	39(2)
C21	1610(6)	3157(4)	2654(3)	53(3)
C22	1456(7)	3666(5)	3048(3)	74(4)
C23	704(7)	4116(5)	3022(4)	75(4)
C24	95(6)	4067(5)	2602(4)	73(4)
C25	238(5)	3557(4)	2207(3)	55(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Neutral-atom scattering factors and anomalous-dispersion corrections for non-hydrogen atoms were taken from ref 8. The hydrogen atoms were placed at calculated positions with isotropic thermal parameters. The perchlorate anion was found to be disordered. This disorder was successfully modeled by a two-site split atom model for the oxygen atoms. Table 2 gives the final atom positional parameters for **1**.

Physical Measurements. Temperature-dependent magnetic susceptibilities of powdered samples of **1** and **2** were recorded on a SQUID magnometer (MPMS, Quantum Design) in the range 2−293 K with an applied field of 1 T. Experimental susceptibility data were corrected for the underlying diamagnetism by using Pascal's constants and for temperature-independent paramagnetism using 60 × 10^{-6} cm^3 mol^{-1} per Cu(II) ion.

Results and Discussion

Synthesis and Structural Characterizations of 1 and 2. The reaction of $CuCl_2 \cdot 2H_2O$ and $CuBr_2$ with piperidinium benzoate and the macrocycle 1,4,7-trimethyl-1,4,7-triazacyclononane (L) in methanol affords, upon addition of $NaClO_4$, green crystals of [{LCuX}$_2$(μ-benzoato)](ClO_4) (X = Cl (**1**), Br (**2**)) in good yields. Figure 1 shows the structure of the dinuclear monocation in crystals of **1**. Table 3 gives selected bond lengths and angles. In the solid state, the cations and perchlorate anions are well separated. The packing between cations and anions or between the cations does not produce any short intermolecular contacts or provide evidence of hydrogen bonding. From this is can be expected that *inter*molecular magnetic exchange interactions between the cations are negligibly small—if at all present.

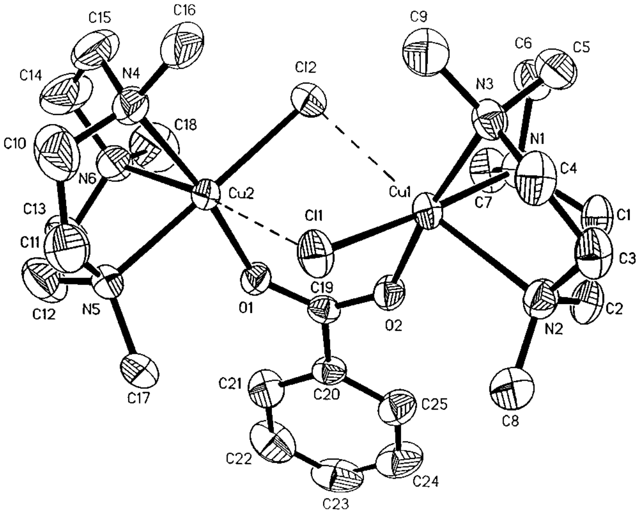

Figure 1. Structure of the monocation in crystals of **1**. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) in the Monocation of **1**

	Bond Lengths		
Cu1−Cl1	2.327(2)	Cu1−O2	1.990(5)
Cu1−N1	2.118(5)	Cu1−N2	2.283(5)
Cu1−N3	2.085(6)	Cu2−Cl2	2.326(2)
Cu2−O1	1.964(4)	Cu2−N4	2.068(6)
Cu2−N5	2.109(5)	Cu2−N6	2.296(6)
Cu1−Cl2	2.885(2)	Cu2−Cl1	2.872(3)
Cu1- - -Cu2	3.565(2)		
	Bond Angles		
Cl1−Cu1−O2	92.6(1)	Cl1−Cu1−N1	176.8(2)
O2−Cu1−N1	89.9(2)	Cl1−Cu1−N2	100.6(2)
O2−Cu1−N2	92.4(2)	N1−Cu1−N2	81.4(2)
Cl1−Cu1−N3	94.0(2)	O2−Cu1−N3	172.0(2)
N1−Cu1−N3	83.6(2)	N2−Cu1−N3	82.1(2)
Cl2−Cu2−O1	91.7(1)	Cl2−Cu2−N4	94.9(2)
O1−Cu2−N4	171.9(2)	Cl2−Cu2−N5	178.6(2)
O1−Cu2−N5	89.4(2)	N4−Cu2−N5	84.1(2)
Cl2−Cu2−N6	99.2(2)	O1−Cu2−N6	92.4(2)
N4−Cu2−N6	82.0(2)	N5−Cu2−N6	81.6(2)
Cu2−O1−C19	135.6(4)	Cu1−O2−C19	135.7(4)
Cu2−Cl2−Cu1	85.6(2)	Cu1−Cl1−Cu2	85.9(2)

The structure of the monocation in **1** (Figure 1) consists of two LCuCl$^+$ moieties which are covalently linked by a symmetric, *syn,syn*-coordinated benzoate bridge. Each of two crystallographically independent cations possesses, within experimental error, C_2 symmetry which is not required crystallographically. The N_3CuClO polyhedron is best described as square-base pyramidal where two amine nitrogens cis to each other, the chloro ligand, and one benzoate oxygen occupy four basal sites and the third amine nitrogen is in the apical position. The *syn,syn*-coordinated benzoate ligand bridges the two basal

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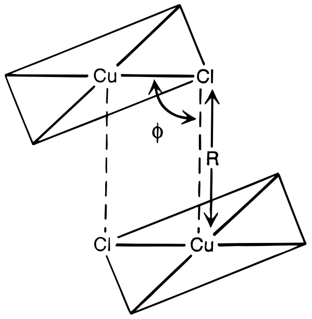
(8) *International Tables for Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 99, 149.

Table 4. Comparison of Structural and Magnetochemical Properties of Carboxylato-Bridged Dicopper complexes

	J, cm^{-1}	α(Cu−O−C), deg	ref
$[Cu_2(CH_3CO_2)_4(py)_2]$	−166	123	2c−e
$[Cu_2(PhCO_2)_4(py)_2]$	−164	123.4	2c
$[Cu_2(CH_3CO_2)_2(phen)_2(H_2O)_2](NO_3)_2\cdot 4H_2O$	−43	128.3	5a
1	−1.2	135.6	this work
2	−2.3		this work

planes of the copper(II) ions and thus connects the (d$_{x^2-y^2}$)^1 magnetic orbitals. For the following discussion, it is important that the Cu−O−C bond angle α increases on going from tetrakis- to bis- to mono(carboxylato)-bridged species (see Table 4). The average Cu−N$_{basal}$ bonds are shorter by 0.19 Å as compared to the Cu−N$_{apical}$ bonds. This difference is typical for all complexes containing an LCu fragment in a square-base pyramidal environment.[9] It is important to notice that the chloro ligand at each of the copper sites (Cu−Cl 2.33 Å) occupies the respective "vacant" sixth coordination site of the other neighboring copper sites, resulting in a long intramolecular Cu···Cl contact of 2.88 Å. Thus the asymmetric arrangement of the Cu_2Cl_2 moiety can be viewed as shown in **A**,which represents a well-known structural motif in many bis(μ-chloro)dicopper(II) complexes.[10] The resulting four-membered Cu_2Cl_2 ring in **1** is not planar.



A

Magnetic Susceptibility Measurements of 1 and 2. Figure 2 displays the temperature dependence (2−295 K) of the molar susceptibility χ_M, and of the magnetic moment, μ_{eff}, of a powdered sample of **1** (for data for **2**, see Supporting Information). A fit of these data to the Bleaney−Bowers equation[1a] yields numerical values for J and g of −1.2 cm^{-1} and 2.24 for **1** and −2.3 cm^{-1} and 2.14 for **2**. Thus, in both cases, a weak antiferromagnetic coupling yielding an $S = 0$ ground state is observed. The values of the singlet−triplet energy gaps, 2J, of **1** and **2** are noticeably smaller than the corresponding values reported for the tetrakis- and bis(μ-carboxylato)-bridged species (Table 4).

For the tetrakis(μ-carboxylato) species, it has been experimentally shown that benzoato- and acetato-bridged complexes have essentially the same magnitude's of spin exchange interaction.[2c] The coupling is also essentially independent of the monodentate apical ligand (pyridine, dimethyl sulfoxide, water, etc.).[1b,c]

However, as indicated by the J values in Table 3, the exchange coupling constant decreases significantly as the number of carboxylate/benzoate bridges decreases from 4 to 1. Furthermore, when one plots the ratio J/n where n is the number of RCO_2^- bridges versus the Cu−O−C angle α an *apparent* linear correlation is observed between these two parameters (Figure 3). The larger α is, the smaller the coupling. This result is consistent with the more general observation that a single *syn,syn*-carboxylate bridge between two paramagnetic transition metal ions (Mn^{2+}, Fe^{2+}) mediates exchange coupling rather poorly.

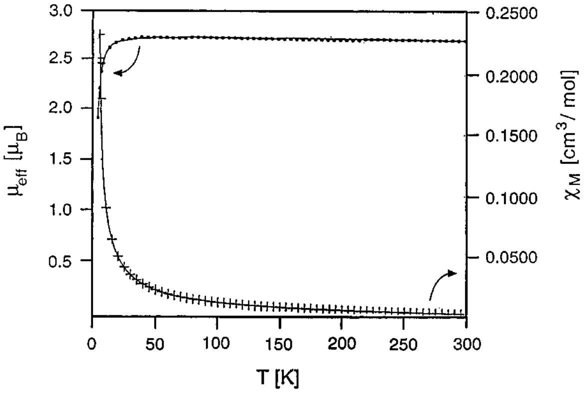


Figure 2. Temperature dependence of the molar susceptibility, χ_M, and of the magnetic moment, μ_{eff}, of **1**. The solid lines represent the best fit of data to the Bleaney−Bowers equation.

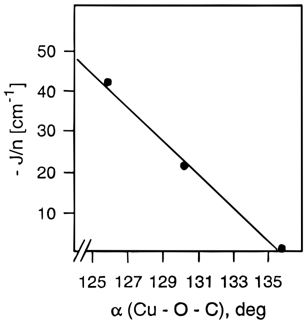


Figure 3. Dependence of J/n (n = number of μ-carboxylates) on the Cu−O−C bond angle α.

Our observations warrant a caveat. It is not at all proven that the observed antiferromagnetic coupling in **1** and **2** actually is propagated through the carboxylate bridge. Hatfield et al. have shown that, in dinuclear bis(μ-chloro)dicopper(II) complexes, a correlation between the structural parameter ϕ/R (**A**) and the coupling constant J exists.[11] From this correlation, a value for J of ∼−5 cm^{-1} may be calculated (ϕ/R for **1** is 29°/Å). This value for J has the correct sign (antiferromagnetic coupling—as observed) and is of similar magnitude. The main structural difference between complexes like $[Cu(tmen)Cl_2]_2$[12] (ϕ/R = 30.76 °/Å, J = −5.6 cm^{-1}) and $[Cu(2\text{-}pic)_2Cl_2]_2$[13] ($\phi/R$ = 29.91 °/Å, J = −7.4 cm^{-1}) and **1** (ϕ/R = 29.9 °/Å, J = −1.2 cm^{-1}) is that the four-membered ring $Cu_2(\mu\text{-}Cl)_2$ is planar in the former species whereas in **1** it is not. It is not known how this structural difference affects the coupling.

In any case, the magnetism of **1** shows that a single *syn,syn*-mono(carboxylate) bridge between two square-base pyramidal copper(II) ions does not provide an effective superexchange pathway, despite the fact that the d$_{x^2-y^2}$ magnetic orbitals of both copper(II) ions are bridged by the benzoate

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[9] Bürger, K.-S.; Chaudhuri, P.; Wieghardt, K.; Nuber, B. *Chem. Eur. J.* **1995**, *1*, 583.

[10] Hatfield, W. E. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willet, R. D., Gatteschi, D., Kahn, O., Eds.; NATO ASI Series, Mathematical and Physical Sciences, Vol. 140; Reidel: Dordrecht, The Netherlands, 1985; p 555.

[11] Marsh, W. E.; Patel, K. C.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1983**, *22*, 511.

[12] Estes, E. D.; Estes, W. E.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 106.

[13] Marsh, W. E.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1982**, *21*, 2679.

group.[14] This is so mainly because the large Cu−O−C angle of 135.6° diminishes the orbital overlap between the metal $d_{x^2-y^2}$ orbital and the p orbital of the oxygen atom of the bridging carboxylate.

Acknowledgment. We thank the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft for financial support.

Supporting Information Available: A plot of χ_M *vs* T for **2** and tables of structure determination details, crystallographic data, expanded non-H atom coordinates, bond lengths, and bond angles, anisotropic thermal parameters for non-H atoms, and calculated positional parameters of H atoms for **1** (10 pages). Ordering information is given on any current masthead page.

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(14) It is noted that, in $[Cu^{II}_2(taec)(\mu\text{-}CH_3CO_2)](ClO_4)_3\cdot 2H_2O$, where taec represents 1,4,8,11-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane, the d_{z^2} orbital of one copper(II) and the $d_{x^2-y^2}$ orbital of the second are bridged by a *syn,anti*-coordinated acetate anion. The magnetism of this species has not been reported, but we anticipate a weak ferromagnetic coupling. Mikuriya, M.; Kida, S.; Murase, I. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1681.