$PtCl_4^{2-}$ and $Pt(CN)_4^{2-}$ might cause the factor of 5 × 10^3 in rate for oxidation of those complexes by HOCl.

Acknowledgment. Thanks are due to I. Lind and B. Jönsson for experimental assistance and to the Swedish Natural Science Research Council for financial support.

Registry No. *trans*-$Pt(CN)_4(OCl)(H_2O)^{2-}$, 96445-84-0; *trans*-$Pt(CN)_4(OCl)(H_2O)^-$, 96445-85-1; $Pt(CN)_4^{2-}$, 15004-88-3; HOCl, 7790-92-3; Cl, 7782-50-5.

Contribution from the Istituto di Chimica Generale e Inorganica, Università di Sassari, 07100 Sassari, Italy, and Dipartimento di Chimica Inorganica e Metallorganica and Centro CNR, Università di Milano, 20133 Milan, Italy

Synthesis, Spectral Properties, and Crystal and Molecular Structure of Tetrakis(μ-2,6-dimethoxybenzoato)diaquadicopper(II) and of Bis(μ-2,6-dimethoxybenzoato)bis(μ-acetato)diaquadicopper(II), a Case of a Dimeric Copper(II) Carboxylate Complex with Mixed Bridges[1]

L. STRINNA ERRE,[2a] G. MICERA,*[2a] P. PIU,[2a] F. CARIATI,[2b] and G. CIANI*[2b]

Received April 30, 1984

The title complexes have been prepared, investigated by single-crystal X-ray analysis, and characterized through magnetic susceptibility and spectroscopic measurements. The tetrakis(μ-2,6-dimethoxybenzoato)diaquadicopper(II) complex (**1**) crystallizes in the orthorhombic space group *Cmca* (No. 64) with cell constants a = 27.890 (7) Å, b = 7.098 (3) Å, c = 19.691 (5) Å, and Z = 4. Least-squares refinement based on 959 significant counter data led to a final conventional R factor of 0.047. The bis(μ-2,6-dimethoxybenzoato)bis(μ-acetato)diaquadicopper(II) complex (**2**) gives monoclinic crystals, space group $P2_1/a$ (No. 14), with a = 7.898 (2) Å, b = 20.334 (6) Å, c = 8.148 (3) Å, β = 101.31 (3)°, and Z = 2. The structure refinement, on the basis of 1479 significant reflections, led to a final conventional R factor of 0.025. The dinuclear compounds have the usual carboxylate quadruply bridged structure, and in complex **2** the groups of the same type act as bridging ligands in mutually trans positions. The copper–copper distance of **2** (2.597 (1) Å) is shorter than that in **1** (2.619 (1) Å) and also shorter than that in copper(II) acetate monohydrate. This fact and the pattern of the other bonding parameters indicate that the molecular framework is rather flexible and can undergo small rearrangements in response to the bonding requirements of the carboxylato ligands or to packing factors. The spectroscopic and magnetic properties of the complexes are interpreted on the basis of the crystal structures. In particular, the complexes exhibit significantly different exchange integrals, $-2J$ (325 and 250 cm^{-1} for **1** and **2**, respectively). The structural and magnetic results are compared with those for a series of related dimers.

Introduction

In the course of an investigation on the interaction of metal ions with humic acid like molecules, we have already described the monomeric complexes formed by 2,6-dihydroxybenzoic acid.[3,4] In order to ascertain the effects of methoxy substitution of the phenolic groups on the coordination behavior of the above salicylic acid like ligand, we have examined the copper(II) complexes of 2,6-dimethoxybenzoic acid (HDMB). Here we describe the structural and spectroscopic properties of two copper(II) acetate like complexes, one of which represents the first recorded example of a dimeric copper(II) carboxylate with mixed bridges.

Experimental Section

Materials. All chemicals were reagent grade. 2,6-Dimethoxybenzoic acid (Merck) was twice recrystallized from water.

Preparation of Complexes. Tetrakis(μ-2,6-dimethoxybenzoato)diaquadicopper(II). Copper(II) nitrate trihydrate (1.6 mmol) and 2,6-dimethoxybenzoic acid (3.2 mmol) were dissolved in ca. 50 mL of water at pH 4. When the solution was allowed to stand at 50 °C, green crystals separated. Anal. Calcd for $C_{18}H_{20}CuO_9$: C, 48.70; H, 4.54; H_2O, 4.06. Found: C, 48.50; H, 4.44; H_2O, 4.0.

When evaporated at room temperature, the solution yielded a green powderlike precipitate that was analyzed as $Cu(DMB)_2 \cdot 1.5H_2O$. Anal. Calcd for $C_{18}H_{21}CuO_{9.5}$: C, 47.73; H, 4.67; H_2O, 5.96. Found: C, 47.60; H, 4.73; H_2O, 6.0.

Bis(μ-2,6-dimethoxybenzoato)bis(μ-acetato)diaquadicopper(II). Copper(II) acetate hydrate (1.6 mmol) and 2,6-dimethoxybenzoic acid (3.2 or 1.6 mmol) were dissolved in 50 mL of water. After slow evaporation at room temperature, the solution yielded a blue powderlike precipitate, which was analyzed as $Cu(DMB)(CH_3COO) \cdot 1.5H_2O$. Anal. Calcd for $C_{11}H_{15}CuO_{7.5}$: C, 39.94; H, 4.57; H_2O, 8.17. Found: C, 39.75; H, 4.47; H_2O, 8.0. By recrystallization from water suitable crystals of the monohydrate complex separated. Anal. Calcd for $C_{11}H_{14}CuO_7$: C, 41.06; H, 4.38; H_2O, 5.59. Found: C, 40.98; H, 4.39; H_2O, 6.0.

Table I. Crystallographic Data

	$[Cu(DMB)_2(H_2O)]_2$ (1)	$[Cu(DMB)(CH_3COO)(H_2O)]_2$ (2)
formula	$C_{36}H_{40}Cu_2O_{18}$	$C_{22}H_{28}Cu_2O_{14}$
fw	887.8	643.5
cryst syst	orthorhombic	monoclinic
space group	*Cmca* (No. 64)	$P2_1/a$ [nonstd setting of $P2_1/c$ (No. 14)]
a, Å	27.890 (7)	7.898 (2)
b, Å	7.098 (3)	20.334 (6)
c, Å	19.691 (5)	8.148 (3)
α, deg	90.0	90.0
β, deg	90.0	101.31 (3)
γ, deg	90.0	90.0
V, Å^3	3898.1	1283.1
ρ_{calcd}, g cm^{-3}	1.513	1.666
Z	4	2
$F(000)$	1832	660
cryst dimens, mm	0.11 × 0.21 × 0.40	0.12 × 0.15 × 0.24
μ(Mo Kα), cm^{-1}	11.67	17.29
ϑ range, deg	3–24	3–24
reflcns measd	$+h,+k,+l$ ($h + k = 2n$)	$\pm h,+k,+l$
no. of reflcns measd	1754	2010
no. of indep reflcns used in struct anal. [$I > 3\sigma(I)$]	958	1479
no. of variable parameters	130	228
weighting p factor[a]	0.04	0.03
R	0.047	0.025
R_w	0.063	0.032
GOF[b]	1.885	1.180

[a] See text. [b] GOF = $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{var})]^{1/2}$.

Analytical and Physical Measurements. Analyses for C and H were performed on a Perkin-Elmer 240 B elemental analyzer. Thermo-

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(1) Part 4 of the series Interaction of Metal Ions with Humic Acid Like Models. Part 3: Micera, G.; Piu, P.; Strinna Erre, L.; Cariati, F.; Pusino, A. *Thermochim. Acta* **1984**, *77*, 67.

(2) (a) Università di Sassari. (b) Università di Milano.

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Table II. Positional Parameters for $[Cu(DMB)_2(H_2O)]_2$, Compound **1**

atom	*x*	*y*	*z*
Cu	0.000	0.1641 (1)	0.03047 (5)
O1	0.0510 (2)	0.2240 (6)	−0.0361 (2)
O2	0.0496 (1)	−0.0540 (5)	−0.0885 (2)
C1	0.0675 (2)	0.1042 (8)	−0.0771 (3)
C2	0.1134 (2)	0.149 (1)	−0.1142 (3)
C3	0.1529 (3)	0.034 (1)	−0.1066 (4)
C4	0.1948 (3)	0.081 (2)	−0.1406 (5)
C5	0.1963 (3)	0.236 (2)	−0.1810 (5)
C6	0.1593 (4)	0.350 (1)	−0.1879 (4)
C7	0.1159 (3)	0.309 (1)	−0.1551 (4)
O3	0.1474 (2)	−0.115 (1)	−0.0660 (3)
C8	0.1840 (4)	−0.242 (2)	−0.0565 (7)
O4	0.0761 (3)	0.4105 (8)	−0.1604 (3)
C9	0.0756 (6)	0.568 (1)	−0.2031 (5)
Ow	0.000	0.4351 (8)	0.0770 (3)

gravimetric curves were obtained with a Perkin-Elmer TGS-2 apparatus under a nitrogen atmosphere at a scanning rate of 2 °C min^{-1}. IR spectra (4000–400 cm^{-1}) were obtained either from Nujol mulls or from powdered samples spread over NaCl plates, with a Perkin-Elmer 683 spectrophotometer. Electronic spectra were obtained on a Beckman Acta M IV spectrophotometer by using the diffuse-reflectance technique with $BaSO_4$ as reference sample. ESR spectra were recorded in X-band (9.15 GHz) on a Varian E 9 spectrometer. Magnetic susceptibilities were measured between 110 and 300 K by the Gouy method on powdered samples under nitrogen, with a Newport Instruments susceptibility system equipped with a cryostatic cooling apparatus. The data were corrected for the diamagnetism of the sample holder and for the temperature-independent paramagnetism of copper. The corrections for diamagnetism were calculated by use of Pascal's constants.

X-ray Data Collection, Structure Determination, and Refinement. The refined cell constants and other relevant crystal data for compounds **1** and **2** are given in Table I, together with details of the intensity measurements. The intensity data were collected on an Enraf-Nonius CAD 4 automated diffractometer, with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å), by the ω-scan method, using variable scan speed (from 2.5 to 20°/min) and a variable scan range of $(1 + 0.35 \tan \vartheta)°$, with a 25% extension at each end for background determination. The intensities of three standard reflections were measured every 2 h of X-ray exposure, and no significant decay was observed for either crystal. The intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied in both cases based on ψ scans (ψ 0–360° every 10°) of suitable reflections with χ values close to 90°; the maximum, minimum, and average relative transmission values were 1.00, 0.88 and 0.95 for **1** and 1.00, 0.92, and 0.97 for **2**, respectively. The structures were solved by conventional Patterson and Fourier methods. Both the dinuclear complexes lie on special positions, complex **1** on a $2/m$ position of the space group *Cmca* (position *a* in Wyckoff notation), with one independent carboxylate which is repeated four times by the local symmetry elements, and complex **2** on an inversion center lying midway between the two copper atoms.

The refinements were carried out by the full-matrix least-squares method. Anisotropic thermal factors were assigned to all non-hydrogen atoms. Difference-Fourier maps showed the locations of all the hydrogen atoms in compound **2**, which were refined isotropically. In compound **1** the positions of various hydrogen atoms were directly observed, but due to the difficulty of convergence in the refinements we have preferred to assume idealized positions for the hydrogen atoms of the ligand (C–H = 0.95 Å, B = 5.0 Å^2), taking into account their contributions to the structure factors, while the water hydrogens were neglected. Weights were assigned according to the formula $w = 4 F_o^2/\sigma(F_o^2)^2$, where $\sigma(F_o^2) = [\sigma(I)^2 + (pI)^2]^{1/2}/LP$ (I and LP being the integrated intensity and the Lorentz–polarization correction, respectively), with p factors of 0.04 (**1**) and 0.03 (**2**).

The final difference Fourier map was rather flat in compound **2**. In compound **1** it showed some residual density not exceeding ca. 0.8 e Å^{-3} close to the water molecule. The final positional parameters are listed in Tables II and III. All computations were performed on a PDP 11/34 computer, using the Enraf-Nonius structure determination package (SDP) and the physical constants therein tabulated.

Results and Discussion

Table III. Positional Parameters for $[Cu(DMB)(CH_3COO)(H_2O)]_2$, Compound **2**

atom	*x*	*y*	*z*
Cu	−0.13311 (4)	0.03069 (2)	0.03405 (4)
O1	0.0807 (3)	0.0209 (1)	−0.2379 (3)
O2	−0.1466 (3)	0.0747 (1)	−0.1807 (3)
C1	−0.0409 (4)	0.0610 (2)	−0.2729 (4)
C2	−0.0623 (5)	0.0952 (2)	−0.4371 (5)
O3	−0.2751 (3)	−0.0431 (1)	−0.0783 (3)
O4	−0.0435 (3)	−0.0947 (1)	−0.1367 (3)
C3	−0.2025 (4)	−0.0891 (1)	−0.1418 (4)
C4	−0.3173 (4)	−0.1417 (2)	−0.2324 (4)
C5	−0.3923 (4)	−0.1327 (2)	−0.4005 (4)
C6	−0.5020 (4)	−0.1803 (2)	−0.4836 (4)
C7	−0.5350 (5)	−0.2358 (2)	−0.4003 (5)
C8	−0.4609 (4)	−0.2463 (2)	−0.2348 (5)
C9	−0.3529 (4)	−0.1982 (2)	−0.1501 (4)
O5	−0.3491 (3)	−0.0760 (1)	−0.4691 (3)
O6	−0.2750 (3)	−0.2013 (1)	0.0146 (3)
C10	−0.4259 (5)	−0.0626 (3)	−0.6407 (5)
C11	−0.3115 (6)	−0.2579 (2)	0.1067 (6)
Ow	−0.3581 (3)	0.0817 (1)	0.0967 (3)
H21	0.031 (7)	0.104 (2)	−0.472 (6)
H22	−0.106 (6)	0.134 (3)	−0.443 (5)
H23	−0.139 (8)	0.081 (4)	−0.488 (9)
H6	−0.557 (4)	−0.175 (2)	−0.588 (4)
H7	−0.611 (4)	−0.269 (2)	−0.458 (5)
H8	−0.486 (4)	−0.284 (1)	−0.178 (4)
H101	−0.541 (4)	−0.065 (2)	−0.653 (4)
H102	−0.380 (5)	−0.020 (2)	−0.662 (5)
H103	−0.398 (7)	−0.100 (3)	−0.720 (7)
H111	−0.441 (5)	−0.261 (2)	0.103 (6)
H112	−0.246 (5)	−0.248 (2)	0.214 (5)
H113	−0.255 (6)	−0.293 (2)	0.079 (6)
Hw1	−0.444 (5)	−0.071 (2)	0.072 (5)
Hw2	−0.345 (6)	0.108 (2)	0.151 (6)

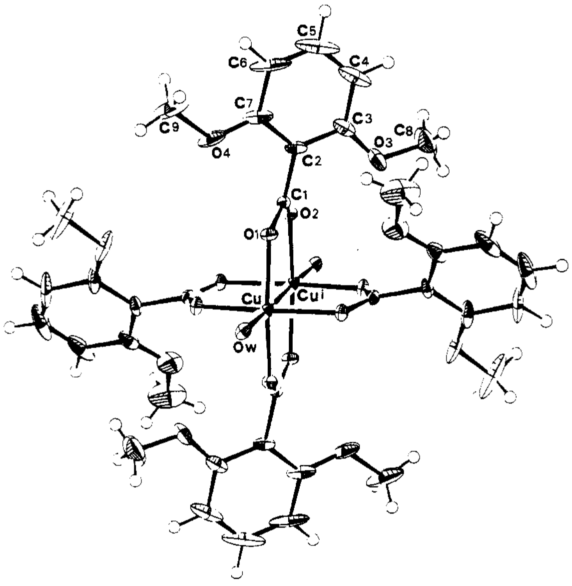

Figure 1. Perspective view of $[Cu(DMB)_2(H_2O)]_2$. Thermal ellipsoids are depicted at the 20% probability level.

Description of Structures. Complexes **1** and **2** both exist as centrosymmetric dinuclear units with four bidentate carboxylate anions forming bridges between the copper atoms (Figures 1 and 2). Complex **1** has a crystallographic C_{2h}-$2/m$ symmetry. In complex **2**, of C_i-$\bar{1}$ symmetry, each pair of carboxylate ligands of the same type occupies mutually trans bridging positions. No experimental evidence was obtained for the existence of the corresponding cis isomer. The coordination sphere of the copper atom in the complexes **1** and **2** is completed by a water molecule bound in the direction of the Cu–Cu axis.

Bond distances and angles are reported in Tables IV and V, for compounds **1** and **2**, respectively. The coordination geometry is that found in a number of dinuclear carboxylate-bridged copper(II) complexes (see, for instance, ref 5). A comparison of mean

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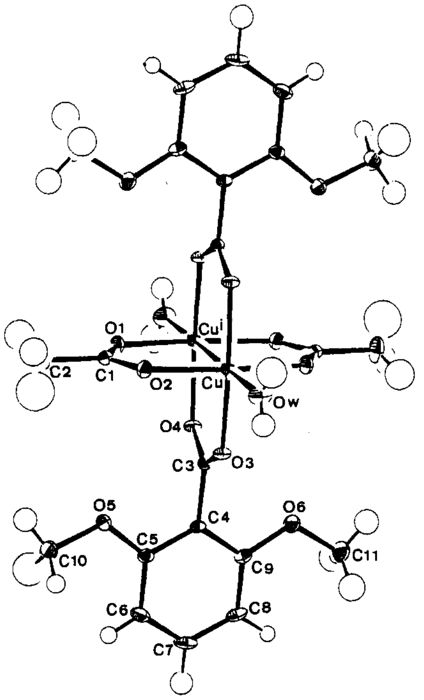

Figure 2. Perspective view of $[Cu(DMB)(CH_3COO)(H_2O)]_2$. Thermal ellipsoids are depicted at the 20% probability level.

Table IV. Interatomic Distances and Angles in $[Cu(DMB)_2(H_2O)]_2$ (**1**)[a]

Distances (Å)			
Cu–Cu^i	2.620 (1)	C3–O3	1.337 (8)
Cu–O1	1.980 (3)	C4–C5	1.358 (16)
Cu–O2^i	1.957 (3)	C5–C6	1.320 (17)
Cu–Ow	2.131 (4)	C6–C7	1.404 (10)
C1–O1	1.260 (5)	C7–O4	1.326 (8)
C1–O2	1.249 (5)	O3–C8	1.374 (10)
C1–C2	1.507 (6)	O4–C9	1.402 (8)
C2–C3	1.377 (8)	O1···Ow^l	2.920 (5)
C2–C7	1.396 (8)	O4···Ow^l	2.899 (6)
C3–C4	1.387 (10)		

Angles (deg)			
Cu^i–Cu–O1	83.6 (1)	O1–C1–O2	125.2 (4)
Cu^i–Cu–O2^i	85.0 (1)	O1–C1–C2	118.6 (4)
Cu^i–Cu–Ow	178.2 (1)	O2–C1–C2	116.1 (4)
O1–Cu–O1^j	91.8 (2)	C1–C2–C3	120.3 (5)
O1–Cu–O2^i	168.5 (1)	C1–C2–C7	119.5 (5)
O1–Cu–O2^k	88.0 (1)	C2–C3–O3	116.1 (5)
O2^i–Cu–O2^k	89.9 (2)	C4–C3–O3	125.2 (8)
O1–Cu–Ow	95.2 (1)	C2–C7–O4	116.5 (5)
O2^i–Cu–Ow	96.3 (1)	C6–C7–O4	124.8 (8)
Cu–O1–C1	122.8 (3)	C3–O3–C8	121.0 (7)
Cu^i–O2–C1	122.4 (3)	C7–O4–C9	119.4 (7)

[a] Superscripts refer to atoms in the following positions: (*i*) $-x, -y, -z$; (*j*) $-x, y, z$; (*k*) $x, -y, -z$; (*l*) $-x, 1 - y, -z$.

Table V. Interatomic Distances and Angles in $[Cu(DMB)(CH_3COO)(H_2O)]_2$ (**2**)[a]

Distances (Å)			
Cu–Cu^i	2.597 (1)	C5–O5	1.353 (4)
Cu–O1^i	1.939 (2)	C6–C7	1.367 (5)
Cu–O2	1.949 (2)	C6–H6	0.89 (3)
Cu–O3	1.987 (2)	C7–C8	1.378 (5)
Cu–O4^i	1.970 (2)	C7–H7	0.96 (4)
Cu–Ow	2.202 (3)	C8–C9	1.388 (4)
C1–O1	1.249 (4)	C8–H8	0.94 (3)
C1–O2	1.259 (4)	C9–O6	1.364 (4)
C1–C2	1.488 (5)	O5–C10	1.437 (5)
C2–H	0.72 (8)–0.86 (6)	O6–C11	1.433 (5)
C3–O3	1.259 (3)	C10–H	0.90 (4)–1.04 (6)
C3–O4	1.253 (3)	C11–H	0.90 (5)–1.02 (5)
C3–C4	1.500 (4)	Ow–Hw1	0.71 (5)
C4–C5	1.393 (4)	Ow–Hw2	0.69 (6)
C4–C9	1.387 (4)	Ow···O3^j	2.977 (4)
C5–C6	1.385 (4)		

Angles (deg)			
Cu^i–Cu–O1^i	82.97 (6)	Cu–O3–C3	119.3 (2)
Cu^i–Cu–O2	86.14 (6)	Cu–O4^i–C3^i	125.1 (2)
Cu^i–Cu–O3	86.89 (6)	O1–C1–O2	125.3 (3)
Cu^i–Cu–O4^i	82.69 (6)	O1–C1–C2	117.2 (3)
Cu^i–Cu–Ow	178.84 (9)	O2–C1–C2	117.5 (3)
O1^i–Cu–O2	169.09 (9)	O3–C3–O4	126.0 (3)
O1^i–Cu–O3	89.57 (9)	O3–C3–C4	116.9 (2)
O1^i–Cu–O4^i	88.81 (9)	O4–C3–C4	117.1 (2)
O2–Cu–O3	90.37 (9)	C3–C4–C5	119.3 (3)
O2–Cu–O4^i	89.28 (9)	C3–C4–C9	120.9 (3)
O3–Cu–O4^i	169.57 (8)	C4–C5–O5	115.2 (3)
O1^i–Cu–Ow	95.9 (1)	C4–C9–O6	114.7 (3)
O2–Cu–Ow	95.0 (1)	C6–C5–O5	125.3 (3)
O3–Cu–Ow	93.1 (1)	C8–C9–O6	124.8 (3)
O4^i–Cu–Ow	97.3 (1)	C5–O5–C10	118.1 (3)
Cu–O1^i–C1^i	125.0 (2)	C9–O6–C11	117.0 (3)
Cu–O2–O1	120.5 (2)	Hw1–Ow–Hw2	116 (6)

[a] Superscripts refer to atoms in the following positions: (*i*) $-x, -y, -z$; (*j*) $-1 - x, -y, -z$.

bond parameters within some dimeric carboxylates is given in Table VI. The values are similar in the various compounds, the small variations being attributable to the bonding ability and steric requirements of the different carboxylates and, possibly, to packing factors.

The coordination about the Cu atom is square pyramidal, neglecting the Cu–Cu interaction and considering only the five bonded oxygen atoms, with the water molecule bond direction almost perpendicular to the plane of the carboxylate oxygens. The metal atoms are displaced in the axial direction toward the water molecules from the oxygen plane, as indicated by the values of the O(carbox)–Cu–O(H_2O) angles, with mean values in the range 95.3–96.3°.

The mean length of the Cu–O(carbox) bond in **1**, 1.968 Å, is almost the same as is observed in $[Cu(CH_3COO)_2(H_2O)]_2$,[6,7] somewhat shorter than the corresponding interaction in the tetrakis(2-bromobenzoate) derivative (1.99 Å),[8] and also shorter than the Cu–O(DMB) mean bond in **2** (1.978 Å). The mean Cu–O(acetate) bond length of 1.944 Å in **2** is significantly shorter than in copper(II) acetate monohydrate.

In compound **2** the bridge lengths, defined as the Cu–O–C–O–Cu distances through the carboxylate bridges, are slightly different for the acetate (6.40 Å) and for DMB (6.47 Å). The Cu–Cu separations in these species are indicative of strong metal–metal interaction, being close to the value of 2.556 Å in metallic copper.[10] The value observed in **1**, 2.620 (1) Å, is not significantly different from that in $[Cu(CH_3COO)_2(H_2O)]_2$. Interestingly, the Cu–Cu bond length in **2**, 2.597 (1) Å, is 0.023 Å shorter than in **1** and 0.017–0.019 Å shorter than in copper(II) acetate hydrate. This is one of the shortest Cu–Cu separations so far observed in Cu(II) dimeric carboxylates, but the trend is difficult to rationalize. It can be suggested that in the "mixed" compound the two acetate anions are allowed to have stronger interaction to the metal ions than in $[Cu(CH_3COO)_2(H_2O)]_2$ because of the favorable competition with the less basic donor DMB ligands. This results in an asymmetric bridge disposition that might be responsible for the observed shortening of the Cu–Cu interaction. We can note (Table VI) that usually a shortening of the Cu–Cu distance is accompanied by a lengthening of the Cu–O(H_2O) bond. Also the Cu–Cu–O(carbox) angles are well

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Table VI. Comparison of the Main Mean Distances (Å) and Angles (deg) within Copper(II) Dimeric Carboxylates

compd	Cu–Cu	Cu–O-(carbox)	Cu–O-(H_2O)	Cu–Cu–O-(H_2O)	Cu–Cu–O-(carbox)	O–Cu–O-(H_2O)	ref
$[Cu(CH_3COO)_2(H_2O)]_2$	2.614 (2)	1.969	2.161 (2)	174.5 (2)	84.4	95.6	6
	2.616 (1)	1.969	2.156 (2)			95.6	7
$[Cu(2\text{-}BrC_6H_4COO)_2(H_2O)]_2$	2.624 (7)	1.99	2.17 (2)	176.5 (7)	84.3	96	8
$[Cu(CH_3CONHCOO)_2(H_2O)]_2$	2.666 (1)	1.971	2.108 (3)	168.8 (1)	83.8	96.3	9
$[Cu(DMB)_2(H_2O)]_2$	2.620 (1)	1.968	2.131 (4)	178.2 (1)	84.3	95.7	this work
$[Cu(DMB)(CH_3COO)(H_2O)]_2$	2.597 (1)	1.944[a] 1.978[b]	2.203 (3)	178.84 (9)	84.7	95.3	this work

[a] Acetate. [b] DMB.

Table VII. Electronic Absorption and Magnetic Data for $[Cu(RCOO)(R'COO)(H_2O)]_2$ Complexes

R	R'	λ_{max}, nm	$g_\parallel$	$g_\perp$	D, cm^{-1}	$-2J$, cm^{-1}	ref
CH_3	CH_3	710	2.35	2.08	0.34	275–305	16–18
DMB	DMB	740	2.36	2.08	0.35	250	this work
DMB	CH_3	675	2.36	2.06	0.34	325	this work

correlated with the M–M distances, according to the trend reported in the literature.[11]

The bond parameters within the carboxylate ligands are normal. In the 2,6-dimethoxybenzoates the presence of α substituents forces the phenyl ring out of coplanarity with respect to the CO_2 plane. In the solid-state structure of the free acid the dihedral angle between the "best planes" is 56.2°.[12] In both compounds **1** and **2** the 11 non-hydrogen atoms of the DMB ligands (with the exception of the two carboxylic oxygens) are nearly coplanar (maximum of the out-of-plane displacement not exceeding ca. 0.05 Å). The dihedral angle of this "best plane" with the CO_2 plane is 58.5° in **1**, close to the value in the free acid. On the other hand, in **2** an increased rotation of the phenyl ring (about the C3–C4 bond) is observed, the above dihedral angle being 87.0°; i.e., the two planes are almost perpendicular. The amount of rotation clearly depends on intramolecular and, possibly, intermolecular nonbonding interactions. As a matter of fact, in compound **1** a dihedral angle close to 90° would give rise to too short contacts among the methoxyl groups of the four ligands.

While in compound **2** the copper atoms are almost coplanar with the CO_2 planes of the four ligands, in **1** a significant displacement (up to 0.37 Å) is present. This is due to a folding of the whole carboxylate about the O1···O2 axis (dihedral angle between the Cu, Cu^i, O1, O2 and C1, O1, O2 planes of 10.4°). Finally, hydrogen bonds involving the water molecules and the oxygen atoms of the carboxylates of adjacent molecules are present in both compounds.

Magnetic and Spectroscopic Results. Temperature-dependent magnetic susceptibility data for $[Cu(DMB)_2(H_2O)]_2$ and $[CuDMB)(CH_3COO)(H_2O)]_2$ are shown in Figure 3. The experimental data are well represented by the usual dimer equation,[13] with the best fit achieved for $g = 2.177$, $2J = -250$ cm^{-1} and $g = 2.230$, $2J = -325$ cm^{-1} for **1** and **2**, respectively.[14] Although it has been demonstrated that the Cu–Cu separation is not the major factor in determining the $2J$ values, a stronger magnetic coupling between the copper centers is associated with a shorter Cu–Cu distance in the acetate–2,6-dimethoxybenzoate complexes.

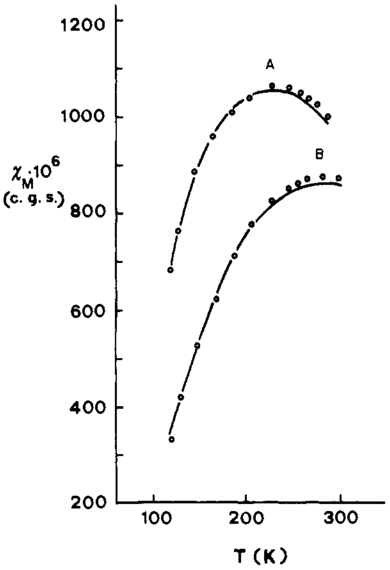

Figure 3. Corrected molar susceptibilities and best-fit curves of $[Cu(DMB)_2(H_2O)]_2$ (A) and $[Cu(DMB)(CH_3COO)(H_2O)]_2$ (B).

The ESR spectra of the complexes, Table VII, are typical of dimeric carboxylates without strong interdimeric exchange, that of **2** exhibiting rhombic distortion for the copper geometry, concordant with the different copper–carboxylate distances.

The reflectance spectra, Table VII, indicate that the energy of the d–d absorption maximum parallels the elongation of the Cu–O(water) axial distance, as expected for chromophores having similar donor sets.

The infrared spectra of the compounds display stretching modes for the carboxylato groups at frequency values near those found for copper(II) acetate hydrate.[19] It is noteworthy that in the spectrum of **2** the absorptions due to the carboxylato group of acetate are not distinguished from the corresponding ones of DMB.

Acknowledgment. This work has been supported by the Italian Ministry of Public Education and the Istituto per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici (CNR, Sassari, Italy). The authors are also grateful to Prof. G. C. Pellacani and Dr. L. Menabue (Department of Chemistry, University of Modena, Modena, Italy) for magnetic measurements and much helpful advice.

Registry No. 1, 96212-88-3; 2, 96212-89-4; Cu, 7440-50-8.

Supplementary Material Available: Listings of thermal parameters for compounds **1** and **2** (Tables A and B), calculated positional parameters for the hydrogen atoms in compound **1** (Table C), and observed and calculated structure moduli for compounds **1** and **2** (20 pages). Ordering information is given on any current masthead page.

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