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Synthesis and X-ray structure of tetrakis[μ-(3,4-dimethoxy-α-β-dihydrocinnamato)] dimethanoldicopper(II)

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The synthesis, magnetic, and structural properties of the title compound are reported. The crystals are triclinic, space group $P\bar{1}$, with $a = 15.084(2)$, $b = 11.820(1)$, $c = 7.5253(7)$ Å, $\alpha = 71.50(1)$, $\beta = 77.61(1)$, $\gamma = 68.68(1)°$ and $Z = 1$; the structure was solved by Patterson and Fourier methods and refined to R 0.0351 for 4147 observed reflections. The content of the unit cell consists of a centrosymmetrical copper acetate-like molecule in which each copper can be described as square-pyramidally surrounded by four carboxylic oxygens in the basal plane [1.955(2)-1.970(2) Å], one methanolic oxygen in the apical site [2.206(2) Å] and a Cu · · · Cu interaction of 2.612(5) Å at a sixth position of a distorted octahedron. The dimers are packed by means of hydrogen bonds formed between the methanolic OH group and the carboxylic O(2) atom of one adjacent complex and by normal Van der Waals contacts. The subnormal magnetic moment, characteristic of exchange interactions between the two copper(II) ions, and the energy of the d–d band observed are consistent with the reported dinuclear copper(II) acetate-like structure.

Introduction

Cinnamic acids are widely distributed in higher plants in the free form and as glucose esters and amides (Burström, 1961); biological activity of some cinnamic acids has already been proved (Goodwin and Mercer, 1983). Pursuing our interest in the interaction of transition metal ions with biologically active ligands, we have already described the coordination behavior of some substituted cinnamic acids with copper(II) (Cabras and Zoroddu, 1986; Zoroddu and Cabras, 1987; Zoroddu and Dallocchio, 1988), but no definite conclusions about their structures were reported. In this paper we describe the synthesis and crystal structure of the title compound.

Experimental

Materials and methods. 3,4-Dimethoxy-α-β-dihydrocinnamic acid (Aldrich Chemie) was used as received; elemental analysis was carried out on a Perkin–Elmer 240B instrument, thermogravimetric determination of MeOH was carried out under air flow on a Perkin–Elmer TGS-2 instrument using a heating rate of 5° min^{-1} in the 25–850°C temperature range. Magnetic susceptibility was determined by using a Bruker-B-MB4 electrobalance at room temperature with Hg|Co(NCS)$_4$| as calibrant and corrected for diamagnetism with the appropriate Pascal constants. Diffuse reflectance electronic spectrum was recorded on a Jasco Uvidec 610 spectrophotometer.

Preparation of the complex

A methanolic solution (15 cc) of $CuCl_2 \cdot 2H_2O$ (0.170 g, 1 mmol) was added dropwise to a solution of the acid (0.210 g, 1 mmol) in the same solvent (15 cc). The pH of the resultant solution was adjusted with some

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drops of aqueous dilute NaOH, upon standing for 1 day, green crystals separated, m.p. 242-243°. Found: C,53.8; H,5.90; MeOH,6.2%. Weight loss in the range 100-140°C. Calc. for $C_{23}H_{30}CuO_9$: C,53.7; H,5.84; MeOH,6.23%. Magnetic moment: $\mu_{eff} = 1.4$ at room temperature. Diffuse reflectance electronic spectrum: $\lambda_{max} = 680$ nm.

Crystallography

Cell parameters and relevant details concerning the structure determination are quoted in Table 1; cell dimensions were obtained by diffractometry and refined using 34 reflections accurately centered. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares with anisotropic thermal parameters; the hydrogen atoms, located from a ΔF map, were isotropically introduced in the last refinement cycle, leading to a *R* factor of 0.0351. Six reflections (2 1 0, 0 0 1, 0 1 1, 1 3 1, $\bar{4}$ 0 1, $\bar{1}$ $\bar{2}$ 1) were excluded from the final refinement as probably affected by extinction or counting errors. The final positional parameters for non-hydrogen atoms are listed in Table 2; the atomic scattering factors were taken from International Tables. All calculations were performed using a GOULD 32/77 Computer and the SHELX program system (Sheldrick, 1976), PARST (Nardelli, 1983), and ORTEP (Johnson, 1965).

Description of the structure

Table 1. Experimental data for the crystallographic analysis

M.W.	1028.06
Formula	$[C_{23}H_{30}CuO_9]_2$
Space group	$P\bar{1}$
a, Å	15.084(2)
b, Å	11.820(1)
c, Å	7.5253(7)
α, °	71.50(1)
β, °	77.61(1)
γ, °	68.68(1)
V, Å^3	1177.8(2)
Z	1
D_c, g cm^{-3}	1.45
D_{obs}, g cm^{-3}	1.47
Reflection for lattice parameters: number	34
Reflection for lattice parameters: θ range	24-40
Crystal data: radiation	Cu−Kα
Crystal data: λ, Å	1.54178
F(000)	538
Temperature, K	294
Crystal size, mm^3	0.54 × 0.66 × 0.70
μ, cm^{-1}	17.03
Diffractometer	Siemens AED
Absorption correction	Not applied
Scan speed, ° min^{-1}	4.0
Scan width, °	1.2 + 0.35tgθ
Radiation	Cu−Kα
θ range	3-70
h range	±17
k range	±13
l range	0, 9
Standard reflection	9 6 2
Max intensity variation	3.8%
Scan mode	$\omega - 2\theta$
No. of measured reflections	4491
Condition for observed reflections	$I > 3\sigma(I)$
No. of reflections used in the refinement	4147
Min max height in final $\Delta\rho$, eÅ^{-3}	−0.54 0.47
No. of refined parameters	418
$R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_0\rvert$	0.0351
$Rw = [\Sigma w(\Delta F)^2/\Sigma wF_0^2]^{1/2}$	0.0394
$S = [\Sigma w(\Delta F)^2/(N - P)]^{1/2}$	2.46
$k, g\ (w = k[\sigma^2(F_0) + gF_0^2]^{-1})$	1.0, 8.48 × 10^{-4}

The structure shows the features of the binuclear copper(II) bridged carboxylates: the molecule is centrosymmetrical (the symmetry centre is located at the middle of the Cu· · ·Cu contact) with four bridging carboxylic groups; each copper can be described as square-pyramidally surrounded by four carboxylic oxygens in the basal plane, one methanolic oxygen in the apical site and a sixth longer position is occupied by the adjacent copper atom. Table 3 reports the more relevant bond distances and angles, these data can be considered as belonging to three classes: (a) the copper–copper interaction; (b) the Cu–O basal bonds, formed by carboxylic oxygens; (c) apical Cu–O bonds. Previously (Melnik, 1982) a survey concerning a large number of these type of carboxylates covering the years up to 1980 found some general trends: the Cu–Cu distance results increased when the acid strength increases and at the same time there is movement of the copper out of the basal plane; the present value of 2.612(5) Å is in the range found in similar compounds, this range, obtained using the results of 53 structural determinations from the Cambridge Structural Database Version 3 (abbreviated as C.S.D.), is 2.563–2.692 Å, mean 2.622 Å. The Cu–O basal bond distances 1.955(2)–1.970(2) Å, only slightly different, agree well with the mean value of 1.966 Å found from the above quoted C.S.D. and the same can be said about the Cu–O apical distance 2.206(2) Å (C.S.D. mean value 2.154 Å, range 2.074–2.398 Å) and strictly similar values are present in

Table 2. Fractional atomic coordinates × 10**^{4}

Atom	*x/a*	*y/b*	*z/c*
CU	46859(2)	48854(3)	17854(4)
O(1)	3430(1)	5471(2)	889(3)
O(2)	3958(1)	5617(2)	−2167(3)
O(3)	−1568(2)	5825(3)	2419(3)
O(4)	−2255(2)	7119(2)	−734(3)
O(5)	4606(1)	6647(2)	1298(3)
O(6)	5144(1)	6842(2)	−1756(3)
O(7)	2126(2)	8681(2)	−5170(4)
O(8)	721(2)	10189(2)	−3648(4)
O(9)	4132(2)	4517(2)	4802(3)
C(1)	3295(2)	5705(2)	−794(4)
C(2)	2283(2)	6070(3)	−1222(4)
C(3)	1529(2)	6682(5)	127(6)
C(4)	516(2)	6834(3)	−154(5)
C(5)	−36(2)	6213(3)	1278(4)
C(6)	−962(2)	6343(3)	1064(4)
C(7)	−1216(4)	5072(5)	4158(6)
C(8)	−1345(2)	7074(3)	−638(4)
C(9)	−2589(3)	7629(5)	−2527(6)
C(10)	−803(2)	7699(3)	−2038(5)
C(11)	120(2)	7577(4)	−1784(5)
C(12)	4845(2)	7259(2)	−330(4)
C(13)	4785(2)	8609(3)	−561(4)
C(14)	4504(2)	9497(3)	−2476(5)
C(15)	3487(2)	9714(3)	−2779(5)
C(16)	3307(2)	9074(3)	−3876(4)
C(17)	2384(2)	9245(3)	−4122(4)
C(18)	2868(3)	8002(4)	−6313(6)
C(19)	1597(2)	10077(3)	−3274(5)
C(20)	−98(3)	11030(5)	−2863(7)
C(21)	1775(3)	10692(3)	−2174(6)
C(22)	2715(3)	10520(3)	−1942(6)
C(23)	3949(3)	3386(4)	5835(5)

Table 3. Selected bond distances (Å) and angles (°)

Cu—O(1)	1.955(2)	Cu—O(5)	1.959(2)
Cu—O(2^{i})	1.969(2)	Cu—O(6^{i})	1.970(2)
Cu—O(9)	2.206(2)	Cu—Cu^{i}	2.612(5)
C(1)—O(1)	1.253(4)	C(12)—O(5)	1.262(3)
C(1)—O(2)	1.276(3)	C(12)—O(6)	1.250(4)
C(1)—C(2)	1.506(4)	C(12)—C(13)	1.520(4)
C(2)—C(3)	1.489(5)	C(13)—C(14)	1.529(4)
C(3)—C(4)	1.526(5)	C(14)—C(15)	1.516(5)
C(6)—O(3)	1.364(4)	C(17)—O(7)	1.368(5)
O(3)—C(7)	1.415(5)	O(7)—C(18)	1.418(5)
C(8)—O(4)	1.371(4)	C(19)—O(8)	1.362(5)
O(4)—C(9)	1.411(5)	O(8)—C(20)	1.424(5)
O(1)—Cu—O(2^{i})	168.91(8)	O(2^{i})—Cu—O(6)	90.29(9)
O(1)—Cu—O(5)	88.64(9)	O(2^{i})—Cu—O(9)	96.14(8)
O(1)—Cu—O(6^{i})	90.13(10)	O(5)—Cu—O(6^{i})	168.98(8)
O(1)—Cu—O(9)	94.93(9)	O(5)—Cu—O(9)	99.25(8)
O(2^{i})—Cu—O(5)	88.84(9)	O(6^{i})—Cu—O(9)	91.77(8)
Cu^{i}—Cu—O(9)	174.23(7)	Cu^{i}—Cu—O(6^{i})	82.65(6)
Cu^{i}—Cu—O(5)	86.33(6)	Cu^{i}—Cu—O(2^{i})	85.39(6)
Cu^{i}—Cu—O(1)	83.67(6)	Cu—O(1)—C(1)	124.7(2)
Cu^{i}—O(2)—C(1)	121.4(2)		
O(1)—C(1)—O(2)	124.7(3)	O(5)—C(12)—O(6)	125.6(2)
O(1)—C(1)—C(2)	117.8(2)	O(5)—C(12)—C(13)	116.9(2)
O(2)—C(1)—C(2)	117.5(2)	O(6)—C(12)—C(13)	117.4(2)
C(1)—C(2)—C(3)	115.1(3)	C(12)—C(13)—C(14)	113.8(2)
C(2)—C(3)—C(4)	113.5(3)	C(13)—C(14)—C(15)	113.5(3)
C(6)—O(3)—C(7)	117.4(4)	C(17)—O(7)—C(18)	117.2(3)
C(8)—O(4)—C(9)	117.0(3)	C(19)—O(8)—C(20)	117.8(3)

$i = 1 - x, 1 - y, \bar{z}$

$Cu(C_6H_5COO)_2(MeOH)$ (Bkouche-Waksman *et al.*, 1980) 2.24(1) Å, in $Cu(acsal)_2$ 2.241(8) Å (Manoilovic-Muir, 1973; acsal = acetylsalicylate) or in $Cu(dpa)_2(dox)_{2.5}$ (Reck and Jähnig, 1979; dpa = 2,4-dichlorophenoxyacetate, dox = 1,4-dioxane) 2.19 Å. The dimensions of the carboxylato cage show some typical values of the CuO_5 chromophore, in fact the sum of all interatomic distances is almost constant and about 11.34 Å (including the half value of the Cu-Cu distance; Melnik, 1982); in agreement the corresponding value in the present work is 11.365 Å. Also the bridging Cu-O-C-O-Cu distances show only small variations: the two independent results 6.453 Å and 6.441 Å are both very similar to 6.44 generally found.

The angles formed by the adjacent oxygens around copper in the basal plane (range 88.64(9)-90.13(10)°) reveal a small distortion: the copper atom is out of the basal plane 0.1883(4) Å toward the O(9) apical oxygen (the range of values generally found was 0.19–0.22 Å), accordingly the angles among the basal oxygens and O(9) are all greater than 90°; the Cu · · · Cu-O(9) angle of 174.23(7)° shows that there is only a little displacement from the linearity. Bond distances and angles in the two organic molecules are strictly similar and show no abnormal features, the C(2)-C(3) and C(13)-C(14) bonds 1.489(5) and 1.529(4) Å seem to be influenced from the sp^2 character of the adjacent carbons. The oxygen atoms of the methoxy groups lie practically in the ring plane, but their methyls are slightly out and oriented in opposite directions probably for minimizing the repulsions among their hydrogens and for packing requirements.

The complex molecules are packed by means of Van der Waals contacts and by the hydrogen bond:

O(9)-H(30)	O(9) · · · O(2)(*x*,*y*,1+*z*)	H(30) · · · O(2)(*x*,*y*,1+*z*)	O(9)-H(30) · · · O(2)(*x*,*y*,1+*z*)
0.80(5) Å	2.888(4) Å	2.11(5) Å	162(4)°

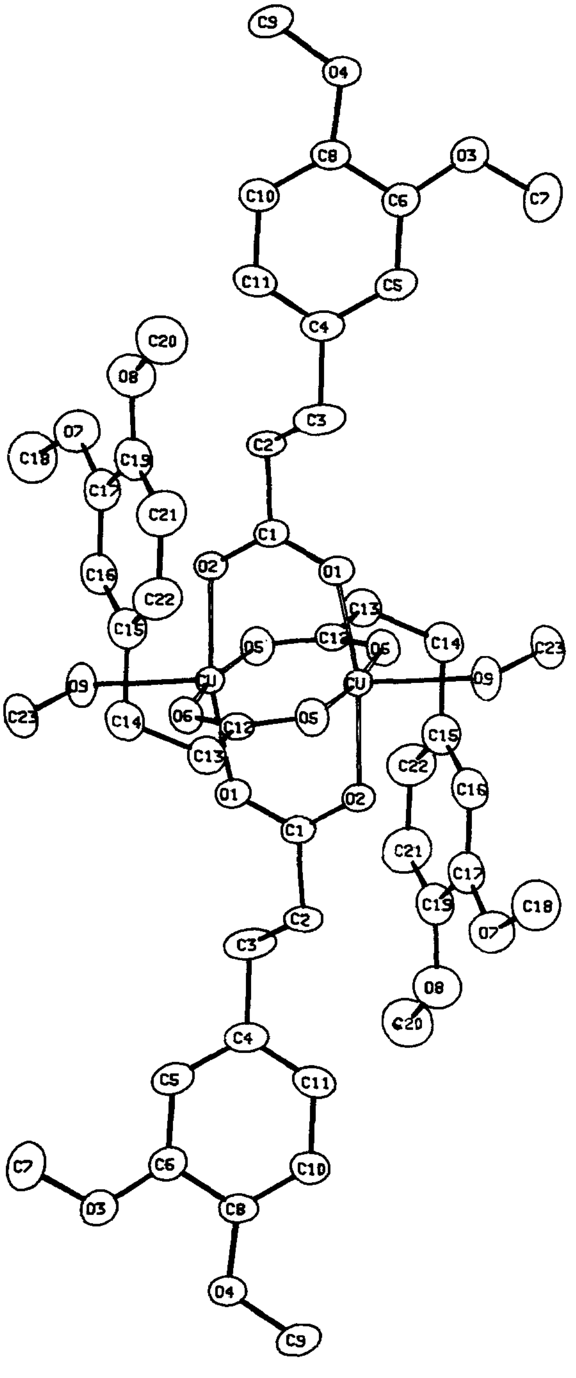

Fig. 1. Perspective view of the dimer.

formed between the methanolic OH group and the carboxylic O(2) of one adjacent complex along the z axis.

The magnetic moment (1.4 B.M.) of the title compound, measured at room temperature, is lower than the spin-only value of 1.73 B.M. and also lower than the value of 1.8 to 2.22 B.M. commonly found for mononuclear copper(II) compounds. The subnormal magnetic moment observed indicates the presence of a magnetic exchange interaction which is typical of antiferromagnetically coupled copper(II) ions, as usually found for a large range of dimeric copper(II) acetate-like complexes (Kato *et al.*, 1964; Smith and Pilbrow, 1974). Furthermore, the value of λ_{max} in the visible region (680 nm) of the reflectance electronic spectrum, indicative of tetragonally copper(II) complex with oxygen donor atoms, is consistent with the observed structure.

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Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication No. 63112 (54 pages).