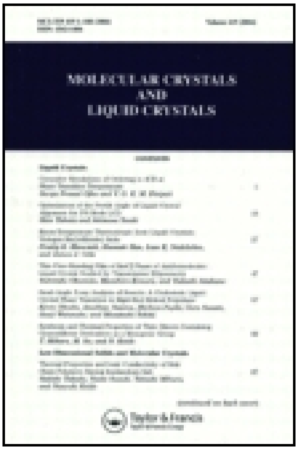

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Crystal and Molecular Structure of an Unreactive Methacrylate Phase, $Cu_2[C_3H_5COO]_4.2[C_3H_5COOH]$

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Version of record first published: 13 Dec 2006.

To cite this article: James W. Shepherd III & Bruce M. Foxman (1986): Crystal and Molecular Structure of an Unreactive Methacrylate Phase, $Cu_2[C_3H_5COO]_4.2[C_3H_5COOH]$, Molecular Crystals and Liquid Crystals, 137:1, 87-99

To link to this article: http://dx.doi.org/10.1080/00268948608070914

Mol. Cryst. Liq. Cryst., 1986, Vol. 137, pp. 87-99
0026-8941/86/1374-0087$20.00/0

Printed in the United States of America

CRYSTAL AND MOLECULAR STRUCTURE OF AN UNREACTIVE METHACRYLATE PHASE, $Cu_2[C_3H_5COO]_4 \bullet 2[C_3H_5COOH]$

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Abstract The title compound was synthesized and its structure determined by single crystal x-ray diffraction techniques. The complex crystallizes in monoclinic space group $P2_1/c$, with a=9.015(2), b=19.704(4), c=9.034(2) Å; β=116.96°, and Z=2. Full-matrix least squares refinement of positional and thermal parameters for all nonhydrogen atoms, using 1682 reflections for which $F>3.92\sigma(F)$, led to R=0.041 and R_w=0.051. Crystals of this material were found to be unreactive upon exposure to x- and γ-irradiation, as well as to heating to 200°C. The lack of reactivity is discussed in terms of carbon-carbon contacts and other factors.

INTRODUCTION

Recently we have described several approaches by which new phases capable of exhibiting solid state reactivity might be generated[1,2]. These approaches derive from two general sources: (i) the "topochemical postulate" advanced by G. M. J. Schmidt[3], and (ii) the immense database of known organic and metal-organic structures. Thus, we have demonstrated[2] that a consideration of the packing of $Ni(H_2O)_4(acetate)_2$ yields the probable packing arrangement for several metal propiolate phases of identical stoichiometry. These propiolate phases were expected, and shown, to exhibit solid state reactivity, since the packing arrangements were characterized by short contacts (3.4-4.1 Å) and parallel acetylene moieties. These qualitative characteristics are those which match the "specifications" of the topochemical postulate.

Ultimately, the understanding of the reactivity --or lack thereof--of a metal carboxylate phase depends upon the determination of structures of such phases, analysis of the intermolecular interactions, and (where appropriate) studies of relative reactivity and product nature. This paper presents an analysis of the intermolecular interactions for a new copper(II) methacrylate phase, which appears to be unreactive.

EXPERIMENTAL

Single crystals of $Cu_2[C_3H_5COO]_4 \cdot 2C_3H_5COOH$ (hereafter 1) were synthesized by addition of methacrylic acid (3.56 g.,0.04 mol, Aldrich) to $CuCO_3$ (2.47 g.,0.02 mol, Mallinkrodt) followed by thorough stirring. Absolute MeOH (75 mL) was then added, and unreacted $CuCO_3$ filtered off. The filtrate was allowed to evaporate in a crystallizing dish covered by a watch glass. After two weeks, a small crop of blue acicular crystals appeared and were removed by filtration (yield 8%). The compound melts with decomposition to a brown solid at about 240°C, but first turns an opaque light green after heating at 200° for five min. Loss of C=O absorption in the IR (1680 cm^{-1}) was observed at this point. The brown solid did not appear to contain polymethacrylate, as evidenced from its IR spectrum. Long exposures to γ-irradiation (^{60}Co) had no effect on the material. The material turns opaque in about one week in air; this appears to be due to sensitivity to moisture with concomitant loss of the coordinated free acid molecules.

A crystal suitable for diffraction work was mounted in a sealed glass capillary. After a satisfactory x-ray photographic study the crystal was tranferred to a Supper No. 455 goniometer and optically centered on a Syntex $P2_1$ diffractometer. Operations were performed as described previously[4]. The analytical scattering factors of Cromer and Waber were used; real and imaginary components of anomalous scattering for Cu were included in the calculations[5]. Details of the structure analysis, in outline form, are presented in Table I. Atomic coordinates and thermal parameters appear in Tables II and III, respectively. A listing of observed and calculated structure amplitudes is available from one of the authors (B. M. F.).

DISCUSSION

The molecular structure of 1 is depicted in Figure 1; the complex has the familiar tetracarboxylatodimetal structure adopted by a large number of $M_2(O_2CR)_4L_2$ compounds. The present structure is most similar to the structure described for the bis(acetic acid) adduct of tetra-μ-acetato-dicopper(II)[6]. Thus, the Cu-Cu distance, 2.602(2) Å, compares well with that in the acetate analogue, 2.582(1) Å. The distance to the axial oxygen atoms in the two structures are equal within experimental error. As in the acetic acid adduct, it is clear from the distances (Table IV) and the location and refinement of the acid H atom that the carbonyl oxygen atom serves as the donor atom

Table I

Data for the X-ray Diffraction Study of $Cu_2[C_3H_5COO]_4 \cdot [C_3H_5COOH]_2$

(A) Crystal Data at 21(1)°C.

Crystal system: monoclinic
Space group: $P2_1/c$ [C^5_{2h} ; no.14]
a = 9.015(2) Å
b = 19.704(4) Å
c = 9.034(2) Å
β = 116.96(2)°
V = 1430.3 $Å^3$

Z = 2
Crystal Size: 0.17 x 0.08 x 0.78 mm.
Formula Wt : 639.6
ρ_{obs} = 1.48(1)[a] g-cm^{-3}
ρ_{calc} = 1.485 g-cm^{-3}
μ = 15.9 cm^{-1} (Mo$K\bar{\alpha}$)

Cell constant determination : 12 pairs of ±(hkl) and refined 2θ, ω, χ values in the range $23 \leq |2\theta| \leq 25°$ (λ(Mo$K\bar{\alpha}$) = 0.71073 Å)

(B) Measurement of Intensity Data

Radiation : Mo$K\bar{\alpha}$, Graphite monochromator
Reflections measured: h, k, ±l (to 2θ = 50°)
Scan type, speed : θ-2θ, variable, 2.09-6.51°/min
Scan range : symmetrical, $[1.6+\Delta(\alpha_2-\alpha_1)]°$
Background measurement : stationary, for 1/4 of scan time at each of the scan limits
No. of reflections measured : 2895; 2533 in unique set
Standard reflections : $1\bar{2}5$, 1 11 1, 411 measured after each 50 reflns; variation < $\pm 3\sigma(I)$ for each
Absorption correction : empirical, using $1\ \bar{1}\ \bar{2}$, $20\bar{6}$, $21\bar{7}$ reflections, normalized transmission factors 0.866-1.000
Statistical information : R_s = 0.030; R_{av} = 0.013 (0kl reflections)
Automatic recentering : after every 1000 reflections

Table I, continued

(C) Solution and Refinement, with 1682 Data for which $F>3.92\sigma(F)$

Weighting of reflections : as before[b], $p = 0.035$
Solution : Patterson, difference-Fourier, routine
Refinement[c] : full-matrix least-squares, with anisotropic temperature factors for Cu, C, O, atoms; isotropic temperature factors for H atoms; all H atoms included as fixed contrib. to F_c except acid H atom; secondary extinction parameter, $g = 2.4(12) \times 10^{-8}$
$R = 0.041$; $R_w = 0.051$; SDU = 1.04
R (structure factor calcn with all 2533 reflections) = 0.078; $R_w = 0.058$
Final difference map : 1 peak, 0.33 $e^-/Å^3$ near Cu; other peaks random and $\leq 0.27 e^-/Å^3$

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[a] Measured by neutral bouyancy in C_6H_6-CCl_4.

[b] Foxman, B. M.; Mazurek H. Inorg. Chem., **1979**, 18, 113 and references therein.

[c] $R_s = \Sigma(\sigma(|F_o|)/\Sigma|F_o|$; $R_{av} = \Sigma|I-I_{av}|/\Sigma I$

$R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $R_w = \{\Sigma w[|F_o|-|F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$

$SDU = \{\Sigma w[|F_o|-|F_c|]^2/(m-n)\}^{1/2}$ where m (=1682) is the number of observations and n (=177) is the number of parameters.

Table II. Atomic Coordinates for 1[a]

Atom	x	y	z
Cu	0.05121(7)	0.04699(3)	0.43286(7)
O(1)	-0.1222(4)	0.0045(2)	0.2245(4)
O(2)	-0.2073(4)	-0.0754(2)	0.3415(4)
O(3)	-0.1233(4)	0.1011(2)	0.4460(4)
O(4)	-0.2096(4)	0.0204(2)	0.5622(4)
O(5)	0.1031(4)	0.1248(2)	0.2867(4)
O(6)	-0.0946(6)	0.0989(3)	0.0360(5)
C(1)	-0.2139(5)	-0.0455(2)	0.2163(5)
C(2)	-0.3383(6)	-0.0697(2)	0.0480(6)
C(3)	-0.3350(8)	-0.0446(3)	-0.0901(7)
C(4)	-0.4575(7)	-0.1200(3)	0.0423(7)
C(5)	-0.2163(6)	0.0794(3)	0.5047(6)
C(6)	-0.3432(6)	0.1263(3)	0.5086(6)
C(7)	-0.4554(8)	0.1035(3)	0.5648(8)
C(8)	-0.3470(8)	0.1942(3)	0.4518(9)
C(9)	0.0294(6)	0.1367(3)	0.1391(6)
C(10)	0.0686(7)	0.1942(3)	0.0594(7)
C(11)	0.2011(9)	0.2361(3)	0.1559(8)
C(12)	-0.0297(11)	0.2044(4)	-0.1099(10)
H(O6)	-0.103(9)	0.068(4)	0.096(9)
H(3A)	-0.4138	-0.0599	-0.1968
H(3B)	-0.2540	-0.0118	-0.0803
H(4A)	-0.4003	-0.1595	0.1003
H(4B)	-0.5214	-0.1021	0.0930
H(4C)	-0.5293	-0.1313	-0.0700
H(7A)	-0.5366	0.1336	0.5672
H(7B)	-0.4505	0.0578	0.6007
H(8A)	-0.3671	0.1934	0.3391
H(8B)	-0.4333	0.2187	0.4607
H(8C)	-0.2432	0.2155	0.5177
H(11A)	0.2283	0.2736	0.1066
H(11B)	0.2645	0.2274	0.2713
H(12A)	-0.1393	0.1886	-0.1406
H(12B)	-0.0331	0.2515	-0.1343
H(12C)	0.0161	0.1802	-0.1704

[a] Numbers in parentheses in this and subsequent tables indicate estimated standard deviations in the least significant digit.

Table III. Thermal Parameters for 1[a]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	0.0445(3)	0.0412(3)	0.0469(3)	-0.0033(3)	0.0180(2)	0.0015(3)
O(1)	0.058(2)	0.054(2)	0.048(2)	-0.013(2)	0.015(2)	-0.002(2)
O(2)	0.055(2)	0.046(2)	0.054(2)	-0.013(2)	0.018(2)	-0.005(2)
O(3)	0.056(2)	0.053(2)	0.076(2)	0.012(2)	0.034(2)	0.009(2)
O(4)	0.055(2)	0.053(2)	0.072(2)	0.004(2)	0.033(2)	0.002(2)
O(5)	0.058(2)	0.052(2)	0.049(2)	-0.010(2)	0.020(2)	0.002(2)
O(6)	0.101(4)	0.098(3)	0.056(3)	-0.050(3)	0.007(2)	0.015(2)
C(1)	0.042(3)	0.040(2)	0.050(3)	0.003(2)	0.016(2)	-0.006(2)
C(2)	0.049(3)	0.041(3)	0.055(3)	0.006(2)	0.014(2)	-0.009(2)
C(3)	0.095(5)	0.082(4)	0.047(3)	-0.023(4)	0.020(3)	-0.014(3)
C(4)	0.065(4)	0.077(4)	0.066(4)	-0.020(3)	0.009(3)	-0.012(3)
C(5)	0.043(3)	0.058(3)	0.044(3)	0.003(3)	0.012(2)	-0.010(3)
C(6)	0.046(3)	0.064(3)	0.057(3)	0.007(3)	0.012(3)	-0.009(3)
C(7)	0.073(4)	0.087(5)	0.106(5)	0.018(4)	0.054(4)	-0.000(4)
C(8)	0.074(5)	0.081(5)	0.106(5)	0.023(4)	0.034(4)	-0.001(4)
C(9)	0.046(3)	0.051(3)	0.059(3)	-0.003(2)	0.024(3)	-0.002(3)
C(10)	0.066(4)	0.054(3)	0.059(3)	-0.000(3)	0.030(3)	0.010(3)
C(11)	0.117(6)	0.071(4)	0.080(4)	-0.037(4)	0.038(4)	0.005(3)
C(12)	0.120(6)	0.105(6)	0.107(6)	-0.011(5)	0.047(5)	0.036(5)
H(O6)	0.11(3)					

[a] Anisotropic thermal parameters are of the form: $\exp[-2\pi^2((a^*)^2 \cdot U_{11} \cdot h^2 + \ldots + 2 \cdot b^* \cdot c^* \cdot U_{23} \cdot k \cdot l)]$. Temperature factors for fixed H atoms were assigned as 1.1•(equivalent isotropic U) of atom to which they are attached.

Table IV. Bond Lengths (Å) and Angles (°) for 1

Cu-Cu	2.602 (2)	C(1)-C(2)	1.501 (7)
Cu-O(1)	2.005 (3)	C(2)-C(3)	1.355 (8)
Cu-O(3)	1.948 (4)	C(2)-C(4)	1.445 (9)
Cu-O(5)	2.207 (3)	C(5)-C(6)	1.483 (8)
O(1)-C(1)	1.266 (6)	C(6)-C(7)	1.396 (10)
O(2)-C(1)	1.253 (6)	C(6)-C(8)	1.427 (9)
O(3)-C(5)	1.253 (7)	C(9)-C(10)	1.468 (8)
O(4)-C(5)	1.264 (7)	C(10)-C(11)	1.387 (9)
O(5)-C(9)	1.214 (6)	C(10)-C(12)	1.392 (10)
O(6)-C(9)	1.314 (7)	O(6)-H(O6)	0.84 (7)

O(1)-Cu-O(3)	88.7 (2)	C(2)-C(1)-O(1)	118.4 (4)
O(1)-Cu-O(2)'	168.9 (2)	C(2)-C(1)-O(2)	118.2 (4)
O(1)-Cu-O(4)'	89.3 (2)	O(1)-C(1)-O(2)	123.4 (5)
O(1)-Cu-O(5)	90.9 (1)	C(3)-C(2)-C(4)	123.0 (5)
O(1)-Cu-Cu'	81.4 (1)	C(3)-C(2)-C(1)	119.9 (5)
O(2)-Cu-O(3)'	90.0 (2)	C(4)-C(2)-C(1)	117.1 (5)
O(2)-Cu-O(4)	89.9 (2)	C(6)-C(5)-O(3)	118.0 (5)
O(2)-Cu-O(5)'	100.2 (1)	C(6)-C(5)-O(4)	117.2 (5)
O(2)-Cu-Cu'	87.6 (1)	O(3)-C(5)-O(4)	124.7 (5)
O(3)-Cu-O(4)'	169.0 (2)	C(7)-C(6)-C(8)	122.0 (6)
O(3)-Cu-O(5)	93.0 (1)	C(7)-C(6)-C(5)	120.1 (5)
O(3)-Cu-Cu'	83.9 (1)	C(8)-C(6)-C(5)	117.9 (5)
O(4)-Cu-O(5)'	97.8 (2)	C(10)-C(9)-O(5)	123.7 (5)
O(4)-Cu-Cu'	85.1 (1)	C(10)-C(9)-O(6)	114.0 (5)
O(5)-Cu-Cu'	171.7 (1)	O(5)-C(9)-O(6)	122.3 (5)
C(1)-O(1)-Cu	126.2 (3)	C(11)-C(10)-C(12)	122.9 (6)
C(1)-O(2)-Cu'	121.4 (3)	C(11)-C(10)-C(9)	118.8 (5)
C(5)-O(3)-Cu	123.6 (4)	C(12)-C(10)-C(9)	118.4 (6)
C(5)-O(4)-Cu'	122.6 (4)	O(6)-H(O6)-O(1)	179 (8)
C(9)-O(5)-Cu	129.3 (3)		

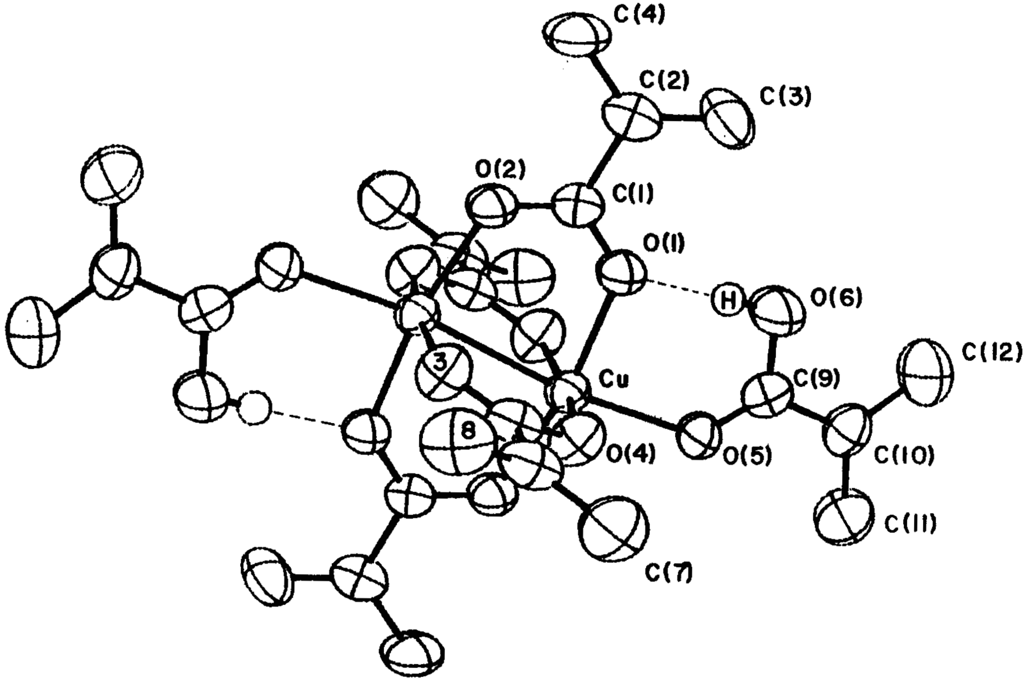

Figure 1. Molecular Structure of 1 showing 50% probability ellipsoids for atoms refined using anisotropic temperature factors. (The H atom attached to O(6) has been assigned an arbitrary radius for clarity.

to copper. The final important structural feature is the near-planarity of the acid ligand and one of the two μ-methacrylato ligands; the dihedral angle between the C(1)-C(2)-C(3)-C(4)-O(1)-O(2) and C(7)-C(8)-C(9)-C(10)-O(5)-O(6) planes is 10.5°. This feature is a consequence of the strong O(6)-H(06)•••O(1) hydrogen bond (O•••O distance, 2.61 Å); the interaction is maximized as the two ligands approach coplanarity. Further, this leads to a significant lengthening of the Cu-O(1) bond relative to the other methacrylate Cu-O bonds (Table IV). This lengthening appears to be present in the structure of the acetic acid analogue, although it was not discussed[6].

Contacts between α- and β′-carbon atoms in the crystal structure of 1 are shown in Figure 2; only those contacts <4.0 Å are shown. The molecules pack in an "interlocking paddle-wheel" fashion. We note that, although short contacts exist, there is no continuous "chain" of parallel contacts which might represent a possible polymerization pathway. Thus, the contacts a (3.86 Å, between C(2) and C(3)′) and b (3.73 Å, between C(3) and C(10)′) are between parallel groups, but are of a "dimeric" type (i. e., no extended chains of contacts are available); contact c (3.92 Å, between C(3) and C(6)′) is also of this type, but the two molecular planes are orthogonal[7]. Thus, this phase shows no reaction on exposure to x- and γ-radiation, and is stable indefinitely in the absence of moisture. [As indicated above, in moist air the coordinated methacrylic acid ligands are replaced by water; it has not been possible to isolate crystals of that material.] Finally, attempts to examine the thermal reactivity of this phase, by analogy with other thermally reactive methacrylates[8], were not successful owing to decomposition of the material

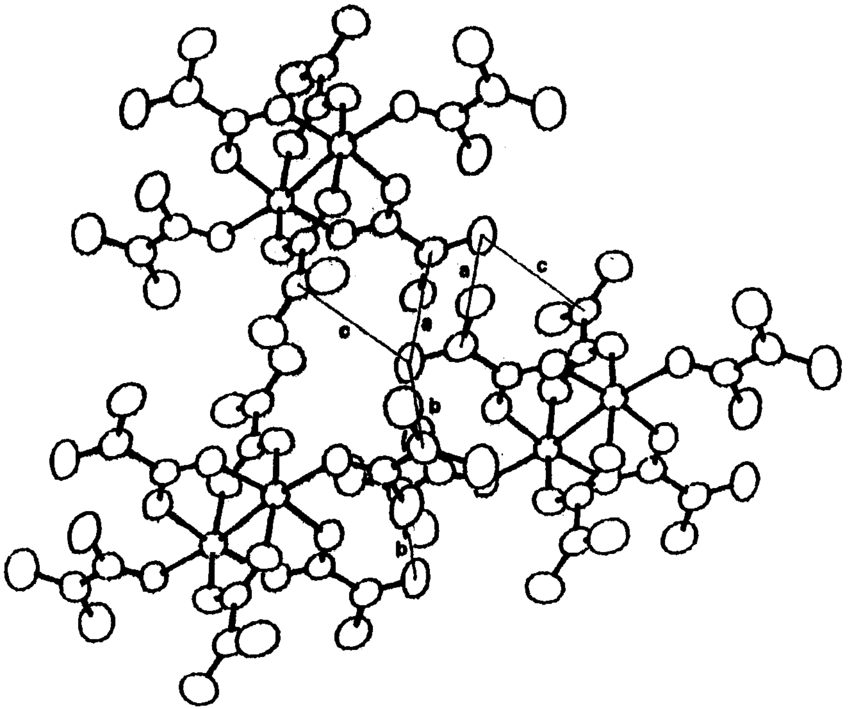

Figure 2. Three molecules of 1 showing important α,β' contacts (see text and footnote 7.

at temperatures >200° C.

While the present results may provide a rationale for the lack of reactivity of this phase, a complete understanding of the influence of structural criteria on reactivity of methacrylates (and other similar materials) depends upon the availabilty of suitable data. Further, appropriate rationales for the behavior of extant cases must also be developed with a view to providing a consistent picture. With these concerns in mind, we are investigating the reactivity and structure of several new methacrylate phases as well as reexamining the intermolecular interactions in the known barium methacrylate phases[9].

Acknowledgements

Acknowledgement is made to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Mazer Fund for undergraduate research at Brandeis University, for the partial support of this research.

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7. Symmetry operations for contacts in text and in Figure 2 are: *a* and *c*: $(1-x,\bar{y},\bar{z})$; *b* : $(\bar{x},\bar{y},\bar{z})$.

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