this steric factor preventing coordination of solvent ligands which, if coordinated, would prevent the formation of polymeric species.

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Structure of Tetrakis[μ-(3,3'-dimethylacrylato)]-bis(ethanol)dicopper(II)

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Abstract. $[Cu_2(C_5H_7O_2)_4(C_2H_6O)_2]$, $M_r = 615{\cdot}7$, triclinic, $P\bar{1}$, $a = 10{\cdot}484$ (2), $b = 12{\cdot}296$ (2), $c = 14{\cdot}303$ (3) Å, $\alpha = 65{\cdot}97$ (1), $\beta = 71{\cdot}69$ (1), $\gamma = 68{\cdot}93$ (1)°, $V = 1540{\cdot}7$ Å^3, $Z = 2$, $D_x = 1{\cdot}327$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}43$ mm^{-1}, $F(000) = 644$, $T = 293$ K, $R = 0{\cdot}042$ for 3398 observed reflections. Centrosymmetric binuclear molecules with four carboxylate bridges spanning a Cu···Cu separation of 2·594 (2) Å are linked to form chains by hydrogen bonding between axial ethanol ligands and the carboxylates. The C=C double bonds of the carboxylate ligands are not involved in coordination of the Cu atoms.

Introduction. A polarographic and potentiometric investigation into the copper(II) complexes formed with a variety of unsaturated carboxylic acids (Resnik & Douglas, 1963) concluded that there was some indication of interaction between copper(II) and the C=C double bond. Edmondson & Lever (1965) presented spectroscopic data for α,β-unsaturated copper(II) carboxylates and tentatively assigned a band at approximately 1500 cm^{-1} in their infrared spectra as a coordinated C=C double-bond stretching mode. Subsequently, several authors have used ESR spectroscopy (Newton & Tabner, 1979), magnetic susceptibility measurements (Zelentsov & Aminov, 1969; Kumar & Suri, 1981) or both techniques (Newton, Oldham & Tabner, 1980; Mrozinski & Heyduk, 1983, 1984; Bukowska-Strzyzewska, Skoweranda, Heyduk & Mrozinski, 1983) to ascertain the exact nature of the bonding in α,β-unsaturated copper(II) carboxylates and their adducts, but no conclusive evidence for the presence of a copper(II)–double-bond interaction has been found. Our work is the first crystallographic investigation into this problem and is also part of a wider study of oligonuclear α,β-unsaturated metal carboxylate complexes.

Experimental. Compound prepared from basic copper carbonate and 3,3'-dimethylacrylic acid in refluxing ethanol, crystals obtained by concentration and cooling. Exposure to air leads to crystal degradation by loss of ethanol. Crystal 0·25 × 0·4 × 0·6 mm mounted in Lindemann capillary, Siemens AED2 diffractometer, cell parameters from 2θ values of 32 reflections measured at $\pm\omega$ ($20 < 2\theta < 22°$). Intensities measured in ω/θ-scan mode, scan width = 1·12° + α-doublet splitting, scan time = 11·6 s, $2\theta_{\max} = 45°$, h −11→0, k −13→13, l −15→15, no significant variation of three standard reflections, no absorption correction. 4016 data (all unique), 3398 with $F > 4\sigma(F)$ for structure determination by Patterson and difference syntheses and blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + 0{\cdot}0002F^2$. Anisotropic thermal parameters for non-H atoms, H atoms constrained [C—H = 0·96 Å, olefinic H on C—C—C external bisectors, rigid methyl groups, H—C—H = 109·5°, $U(\mathrm{H}) = 1{\cdot}2U_{\mathrm{eq}}(\mathrm{C})$; O-H atoms freely refined], isotropic extinction parameter $x = 1{\cdot}5\ (2) \times 10^{-6}$ $[F_c' = F_c/(1+xF_c^2/\sin 2\theta)^{1/4}]$. 364

parameters, $R = 0{\cdot}042$, $wR = 0{\cdot}048$, slope of normal probability plot = 1·82, mean $\Delta/\sigma = 0{\cdot}03$, max. = 0·3 for methyl-group rotations, $\Delta\rho_{\max} = 0{\cdot}37$, $\Delta\rho_{\min} = -0{\cdot}50$ e Å^{-3}. Scattering factors from *International Tables for X-ray Crystallography* (1974). Programs: *SHELXTL* (Sheldrick, 1985).

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* (Å^2 × 10^3)

$U_{\rm eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	$U_{\rm eq}$
Cu(1)	5733·4 (5)	5075·6 (5)	543·7 (4)	44·7 (2)
Cu(2)	5314·7 (5)	4307·1 (4)	4437·3 (3)	38·8 (2)
O(11)	4800 (3)	3888 (3)	1735 (2)	56 (2)
O(12)	3543 (3)	3786 (3)	794 (2)	61 (2)
C(11)	3904 (4)	3493 (4)	1636 (3)	48 (2)
C(12)	3257 (5)	2656 (4)	2596 (3)	62 (2)
C(13)	2441 (5)	1985 (4)	2698 (4)	74 (3)
C(14)	2062 (7)	1900 (6)	1819 (5)	114 (5)
C(15)	1879 (8)	1203 (6)	3764 (5)	129 (5)
O(21)	4103 (3)	6420 (3)	771 (2)	59 (2)
O(22)	2844 (3)	6305 (3)	−167 (2)	63 (2)
C(21)	3027 (4)	6759 (4)	420 (3)	51 (2)
C(22)	1841 (4)	7768 (4)	679 (3)	55 (2)
C(23)	1756 (5)	8415 (4)	1248 (3)	59 (2)
C(24)	2879 (6)	8265 (5)	1751 (4)	81 (3)
C(25)	441 (6)	9406 (5)	1427 (5)	92 (3)
O(31)	6947 (3)	5298 (3)	1390 (2)	64 (2)
C(31)	8403 (5)	4977 (8)	1215 (5)	123 (5)
C(32)	9118 (7)	5468 (11)	1421 (8)	244 (11)
O(41)	3381 (3)	5083 (3)	4271 (2)	54 (2)
O(42)	2827 (3)	6269 (3)	5246 (2)	59 (2)
C(41)	2545 (4)	5882 (4)	4660 (3)	47 (2)
C(42)	1127 (4)	6437 (4)	4443 (3)	58 (2)
C(43)	544 (4)	6204 (4)	3872 (3)	61 (2)
C(44)	1253 (5)	5296 (5)	3304 (4)	78 (3)
C(45)	−950 (5)	6860 (5)	3773 (5)	92 (4)
O(51)	5827 (3)	5738 (3)	3263 (2)	51 (1)
O(52)	5266 (3)	6927 (2)	4234 (2)	56 (1)
C(51)	5665 (4)	6756 (4)	3368 (3)	46 (2)
C(52)	5983 (4)	7770 (4)	2403 (3)	59 (2)
C(53)	6009 (5)	8884 (4)	2300 (4)	73 (3)
C(54)	5823 (7)	9312 (5)	3165 (5)	109 (4)
C(55)	6303 (7)	9795 (6)	1209 (5)	125 (4)
O(61)	5803 (3)	3143 (3)	3514 (2)	66 (2)
C(61)	6578 (7)	1885 (6)	3793 (6)	126 (5)
C(62)	7782 (9)	1564 (8)	3185 (8)	217 (9)

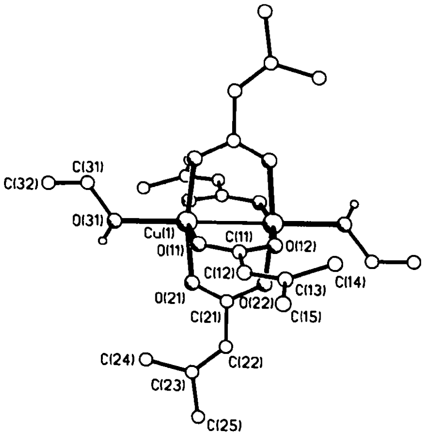

Fig. 1. One of the binuclear molecules, showing the atom labelling; constrained H atoms are omitted.

Discussion. The final atomic parameters are listed in Table 1.* The structure consists of two independent centrosymmetric binuclear copper(II) units (Fig. 1) linked by hydrogen bonds to form infinite chains (Fig. 2) [O(51)···O(31) 2·755; O(61)···O(11) 2·741 Å]. As can be seen from the list of bond lengths and angles (Table 2) there are slight structural variations between the two binuclear units, but these are not chemically significant

Table 2. *Bond lengths* (Å) *and angles* (°)

Cu(1)–Cu(1$^{\rm i}$)	2·601 (2)	Cu(2)–Cu(2$^{\rm ii}$)	2·586 (1)
Cu(1)–O(11)	1·987 (3)	Cu(2)–O(41)	1·951 (3)
Cu(1)–O(21)	1·954 (3)	Cu(2)–O(51)	1·977 (3)
Cu(1)–O(31)	2·156 (4)	Cu(2)–O(61)	2·154 (4)
Cu(1)–O(12$^{\rm i}$)	1·966 (3)	Cu(2)–O(42$^{\rm ii}$)	1·950 (3)
Cu(1)–O(22$^{\rm i}$)	1·954 (3)	Cu(2)–O(52$^{\rm ii}$)	1·968 (3)
O(11)–C(11)	1·267 (7)	O(41)–C(41)	1·250 (5)
O(12)–C(11)	1·248 (6)	O(42)–C(41)	1·264 (7)
C(11)–C(12)	1·473 (5)	C(41)–C(42)	1·470 (6)
C(12)–C(13)	1·329 (9)	C(42)–C(43)	1·324 (9)
C(13)–C(14)	1·483 (12)	C(43)–C(44)	1·490 (8)
C(13)–C(15)	1·498 (8)	C(43)–C(45)	1·505 (6)
O(21)–C(21)	1·244 (6)	O(51)–C(51)	1·267 (6)
O(22)–C(21)	1·269 (7)	O(52)–C(51)	1·255 (6)
C(21)–C(22)	1·482 (6)	C(51)–C(52)	1·477 (5)
C(22)–C(23)	1·317 (8)	C(52)–C(53)	1·326 (8)
C(23)–C(24)	1·485 (9)	C(53)–C(54)	1·466 (11)
C(23)–C(25)	1·508 (6)	C(53)–C(55)	1·519 (7)
O(31)–H(31)	0·755 (41)	O(61)–H(61)	0·793 (44)
O(31)–C(31)	1·398 (6)	O(61)–C(61)	1·417 (6)
C(31)–C(32)	1·273 (18)	C(61)–C(62)	1·318 (11)
O(11)–Cu(1)–O(21)	89·0 (1)	O(41)–Cu(2)–O(51)	88·5 (1)
O(11)–Cu(1)–O(31)	97·6 (1)	O(41)–Cu(2)–O(61)	96·1 (1)
O(21)–Cu(1)–O(31)	95·6 (1)	O(51)–Cu(2)–O(61)	95·9 (1)
O(11)–Cu(1)–Cu(1$^{\rm i}$)	85·0 (1)	O(41)–Cu(2)–Cu(2$^{\rm ii}$)	83·2 (1)
O(21)–Cu(1)–Cu(1$^{\rm i}$)	83·0 (1)	O(51)–Cu(2)–Cu(2$^{\rm ii}$)	84·9 (1)
O(31)–Cu(1)–Cu(1$^{\rm i}$)	177·0 (1)	O(61)–Cu(2)–Cu(2$^{\rm ii}$)	178·9 (1)
O(11)–Cu(1)–O(12$^{\rm i}$)	169·0 (2)	O(41)–Cu(2)–O(42$^{\rm ii}$)	169·3 (2)
O(21)–Cu(1)–O(12$^{\rm i}$)	90·2 (1)	O(51)–Cu(2)–O(42$^{\rm ii}$)	90·1 (1)
O(31)–Cu(1)–O(12$^{\rm i}$)	93·4 (1)	O(61)–Cu(2)–O(42$^{\rm ii}$)	94·6 (1)
Cu(1$^{\rm i}$)–Cu(1)–O(12$^{\rm i}$)	84·0 (1)	Cu(2$^{\rm ii}$)–Cu(2)–O(42$^{\rm ii}$)	86·2 (1)
O(11)–Cu(1)–O(22$^{\rm i}$)	89·6 (1)	O(41)–Cu(2)–O(52$^{\rm ii}$)	90·7 (1)
O(21)–Cu(1)–O(22$^{\rm i}$)	169·0 (2)	O(51)–Cu(2)–O(52$^{\rm ii}$)	169·4 (2)
O(31)–Cu(1)–O(22$^{\rm i}$)	95·4 (1)	O(61)–Cu(2)–O(52$^{\rm ii}$)	94·7 (1)
Cu(1$^{\rm i}$)–Cu(1)–O(22$^{\rm i}$)	86·1 (1)	Cu(2$^{\rm ii}$)–Cu(2)–O(52$^{\rm ii}$)	84·5 (1)
O(12$^{\rm i}$)–Cu(1)–O(22$^{\rm i}$)	89·0 (1)	O(42$^{\rm ii}$)–Cu(2)–O(52$^{\rm ii}$)	88·6 (1)
Cu(1)–O(11)–C(11)	122·1 (2)	Cu(2)–O(41)–C(41)	125·0 (4)
C(11)–O(12)–Cu(1$^{\rm i}$)	124·9 (3)	C(41)–O(42)–Cu(2$^{\rm ii}$)	121·2 (2)
O(11)–C(11)–O(12)	124·0 (4)	O(41)–C(41)–O(42)	124·4 (4)
O(11)–C(11)–C(12)	116·1 (4)	O(41)–C(41)–C(42)	119·9 (5)
O(12)–C(11)–C(12)	119·8 (5)	O(42)–C(41)–C(42)	115·7 (4)
C(11)–C(12)–C(13)	128·8 (5)	C(41)–C(42)–C(43)	128·8 (4)
C(12)–C(13)–C(14)	124·9 (5)	C(42)–C(43)–C(44)	125·0 (4)
C(12)–C(13)–C(15)	119·6 (6)	C(42)–C(43)–C(45)	120·2 (5)
C(14)–C(13)–C(15)	115·4 (6)	C(44)–C(43)–C(45)	114·8 (6)
Cu(1)–O(21)–C(21)	125·2 (4)	Cu(2)–O(51)–C(51)	122·8 (2)
C(21)–O(22)–Cu(1$^{\rm i}$)	120·9 (3)	C(51)–O(52)–Cu(2$^{\rm ii}$)	124·1 (3)
O(21)–C(21)–O(22)	124·8 (4)	O(51)–C(51)–O(52)	123·5 (3)
O(21)–C(21)–C(22)	119·9 (5)	O(51)–C(51)–C(52)	116·4 (4)
O(22)–C(21)–C(22)	115·3 (4)	O(52)–C(51)–C(52)	120·1 (5)
C(21)–C(22)–C(23)	128·2 (5)	C(51)–C(52)–C(53)	128·7 (5)
C(22)–C(23)–C(24)	125·3 (4)	C(52)–C(53)–C(54)	125·2 (4)
C(22)–C(23)–C(25)	120·1 (5)	C(52)–C(53)–C(55)	118·8 (6)
C(24)–C(23)–C(25)	114·7 (5)	C(54)–C(53)–C(55)	116·0 (5)
Cu(1)–O(31)–H(31)	117·0 (39)	Cu(2)–O(61)–H(61)	114·7 (32)
Cu(1)–O(31)–C(31)	125·7 (5)	Cu(2)–O(61)–C(61)	124·4 (4)
H(31)–O(31)–C(31)	115·0 (36)	H(61)–O(61)–C(61)	120·8 (33)
O(31)–C(31)–C(32)	125·4 (8)	O(61)–C(61)–C(62)	118·5 (6)

Symmetry operators: (i) $1-x$, $1-y$, $-z$; (ii) $1-x$, $1-y$, $1-z$.

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* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43165 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

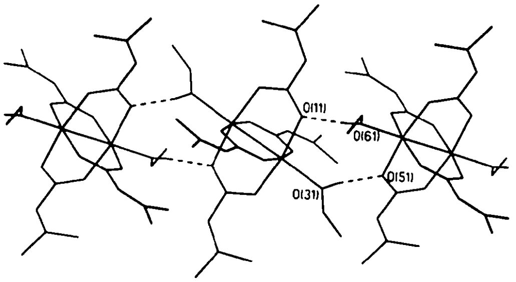

Fig. 2. The hydrogen bonding between ethanol and carboxylate ligands.

and, unless otherwise stated, structural parameters quoted below are averages over all relevant ligands in both dimers.

The metal separation [2·594 (2) Å] is within the normal range for tetrakis(μ-carboxylato)-dicopper(II) complexes; the Cu atoms lie 0·185 Å from the plane (r.m.s. $\Delta = 0{\cdot}002$ Å) defined by their four coordinating carboxylate O atoms, displaced towards the axial ethanol ligands. The bidentate 3,3′-dimethylacrylate bridges are slightly distorted; Cu—O bonds involving O atoms participating in intermolecular hydrogen bonding are approximately 0·02 [O(51)] and 0·03 Å [O(11)] larger than the other Cu—O bonds [1·957 (3) Å]. Distortion of this type and magnitude has been reported for tetrakis(μ-acetato)-bis(methanol)dicopper(II) (Rao, Sathyanarayana & Manohar, 1983) in which binuclear copper(II) units also link *via* intermolecular hydrogen bonding to form chains. The Cu—O(alcohol) bond lengths for that complex [2·160 (3) Å] and for tetrakis[μ-(2,2,5,5-tetramethyl-1-oxo-dihydropyrrole-3-carboxylato)]-bis(ethanol)dicopper(II) (2·17 Å) (Gusejnova & Mamedov, 1978) show close agreement with the values presented here [2·155 (4) Å]. This is expected since the coordination geometry around the Cu atom in each complex approximates to square pyramidal; the bond lengths are roughly 0·35 Å shorter than those between Cu^{II} and O(ethanol) where the ethanol molecule forms part of an axially distorted octahedral coordination sphere around the Cu^{II} (Muhonen, Pajunen & Hämäläinen, 1980).

There is no coordination of the carboxylate side-chain double bonds to the Cu atoms, and no significant intermolecular double-bond interaction.

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Structure of Diformatobis(2-methylbenzimidazole)copper(II)

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Abstract. $[Cu(CHO_2)_2(C_8H_8N_2)_2]$, $M_r = 417{\cdot}91$, monoclinic, $P2_1/n$, $a = 6{\cdot}3306$ (5), $b = 13{\cdot}4855$ (11), $c = 11{\cdot}1863$ (5) Å, $\beta = 105{\cdot}471$ (5)°, $V = 920{\cdot}4$ Å^3, $Z = 2$, $D_x = 1{\cdot}508$, $D_m = 1{\cdot}515$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·541840 Å, $\mu = 1{\cdot}91$ mm^{-1}, $F(000) = 430$, room temperature, final $R = 0{\cdot}0391$ for 1877 reflections. The