Crystal Structure and Magnetic Properties of Tetrakis(μ-crotonato)bis-(quinoline)dicopper(II)

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The compound $Cu_2(CH_3CHCHCOO)_4quin_2$ was synthesized at room temperature and its crystal and molecular structures were solved. It crystallizes in the space group $P2_1/n$. The lattice constants are: $a = 14.594(1)$, $b = 10.863(1)$, $c = 10.581(1)$ Å and $\beta = 99.52°$. The Cu–Cu distance across the dimeric unit is 2.660(3) Å with Z = 2. Least squares refinement of the structure led to a conventional weighted R factor of 0.055. The temperature dependence of the molar susceptibility, studied in the range 80–300 K, revealed antiferromagnetic coupling characterized by a -333 cm^{-1} singlet–triplet separation. The EPR spectrum of a polycrystalline sample of the compound showed triplet-state transitions, characterized by $|D|$ and E parameters equal to 0.388 cm^{-1} and 0.0053 respectively.

Introduction

Copper(II) dimers, including the copper(II) carboxylates, have for many years been the subject of intensive studies because of their interesting properties. Recently, new data about the correlation of physicochemical parameters of copper(II) carboxylates, the pK_a values of bridging and axial ligands, and structural parameters have been reported [1–7].

Relatively little is known about the dimeric copper(II) carboxylates, containing the anions of unsaturated aliphatic carboxylic acids as the bridge ligands [8–11].

An interesting correlation was observed for the dimeric copper(II) acetates and halogenoacetates, connected with elongation of the Cu–Cu distance when the pK_a of the bridge ligand decreased [12]. Obviously the axial ligands also have influence upon the distance between the interacting magnetic centers [13].

The present paper should be regarded as the beginning of our studies on the relation of the structural parameters and pK_a values of ligands to the magnetic and spectroscopic properties of copper(II) dimers with α,β-unsaturated carboxylic bridging ligands.

Experimental

Tetrakis(μ-crotonato)dicopper(II) was dissolved in methanol and quinoline was added in small excess over the equimolar amount. The solution was heated under reflux. The methanol in excess was distilled off and the solution was set aside for crystallization. After 24 hours the crystals of crotonate quinoline adduct were filtered off. The yield was about 30%. The product was recrystallized from the hot methanol, washed with cold methanol and dried in a vacuum desiccator over anhydrous calcium chloride. *Anal.* Calcd. for $C_{34}H_{34}N_2O_8Cu_2$: C, 56.20; H, 4.69; N, 3.87; Cu, 17.51%. Found: C, 56.71; H, 4.77; N, 4.16; Cu, 17.20%.

Crystal Structure and Refinement

Space group and preliminary cell constants were determined by oscillation and Weissenberg photographs. Accurate unit cell parameters were obtained by least-squares refinement of the θ values of 20

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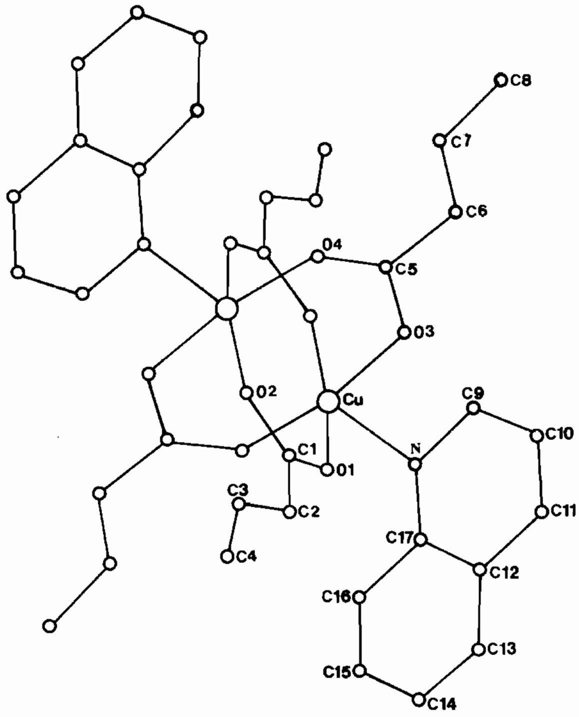

Fig. 1. A view of the binuclear molecule.

reflections measured on a diffractometer. The calculated density of 1.467 g cm^{-3} for $Z = 2$ agrees well with the value of 1.45 g cm^{-3} obtained by the flotation method. Intensity data were measured by the $\theta - 2\theta$ scan technique on a $P2_1$-Syntex four-circle diffractometer with graphite-monochromated CuK_{α} radiation. The size of the crystal used was 0.20 × 0.20 × 0.30 mm; 1831 independent reflections with $|F_o| > 3\sigma|F_o|$ collected up to $\sin\theta/\lambda = 0.59$ Å^{-1} were used in the subsequent calculations. Corrections were made for Lorentz and polarization effects, but not for absorption.

The structure was solved by the heavy-atom method. The coordinates of the copper atom were found from a three-dimensional Patterson synthesis and those of all the other non-hydrogen atoms were taken from the subsequent Fourier synthesis. Several cycles of block-diagonal least-squares refinement using isotropic thermal parameters brought the R value to 0.15. The hydrogen atoms were located from geometrical considerations assuming C–H to be 1.0 Å. They were included in further calculations with isotropic thermal parameters but were not refined. After further cycles of block-diagonal least squares refinement with anisotropic temperature factors for non-hydrogen atoms, R dropped to 0.055.

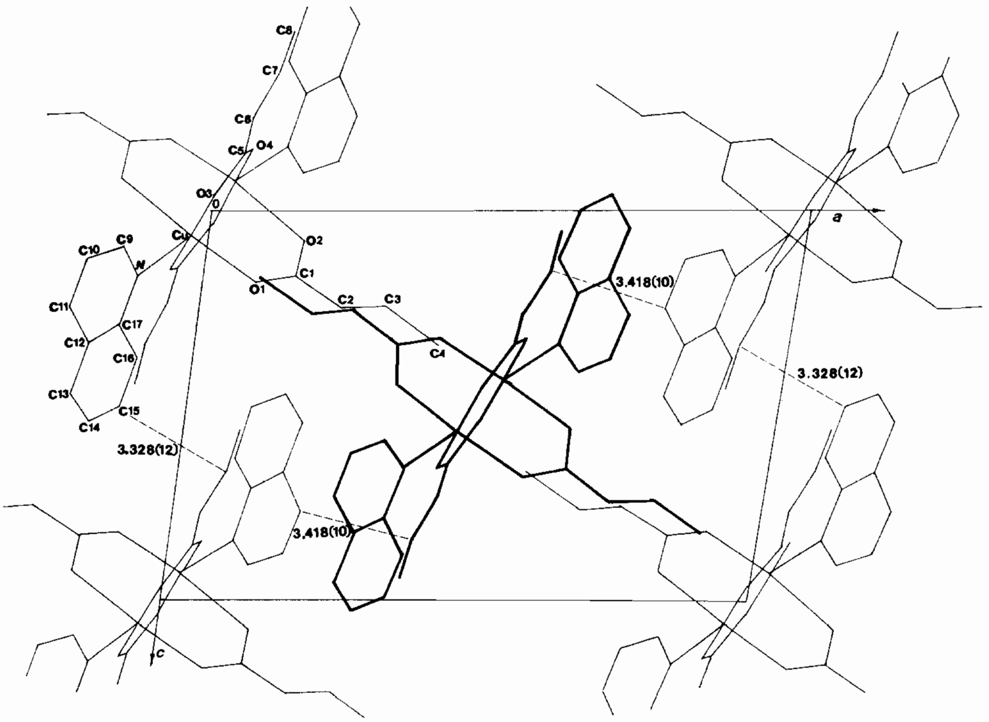

Fig. 2. Molecular packing.

TABLE I. Final Atomic Coordinates (fractional, ×10^4) and Thermal Anisotropic Parameters.[a]

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	−351(1)	823(1)	719(1)	37(1)	56(1)	61(1)	1(1)	13(1)	−4(1)
O(1)	878(3)	839(4)	1823(4)	32(2)	77(4)	59(4)	5(3)	−2(2)	−18(4)
O(2)	1447(3)	−555(4)	620(4)	29(2)	75(4)	61(4)	4(3)	0(2)	−16(4)
O(3)	87(3)	2033(4)	−429(4)	46(2)	43(4)	68(4)	−3(3)	27(3)	−3(3)
O(4)	666(3)	648(4)	−1642(4)	53(3)	44(4)	69(4)	1(3)	33(3)	7(3)
N(1)	−1101(3)	2247(4)	1653(4)	27(2)	49(5)	53(5)	1(3)	12(3)	−9(4)
C(1)	1510(4)	154(5)	1561(5)	32(3)	45(5)	49(5)	−5(3)	10(3)	17(4)
C(2)	2414(4)	200(6)	2449(6)	35(3)	62(6)	47(5)	−1(4)	2(3)	0(5)
C(3)	3076(4)	−598(6)	2405(6)	38(4)	76(7)	65(6)	−8(4)	6(4)	1(5)
C(4)	3999(5)	−645(8)	3275(8)	40(4)	123(9)	114(9)	17(5)	−11(5)	1(8)
C(5)	454(4)	1720(5)	−1384(5)	25(3)	49(5)	57(6)	−3(3)	1(3)	7(5)
C(6)	621(4)	2732(6)	−2271(6)	41(4)	56(6)	80(7)	−5(4)	15(4)	12(5)
C(7)	848(5)	2505(7)	−3406(6)	48(4)	86(7)	67(6)	−14(5)	11(4)	23(6)
C(8)	954(7)	3484(9)	−4377(8)	91(6)	138(9)	91(9)	−37(7)	10(6)	55(8)
C(9)	−1444(4)	3131(6)	868(6)	36(3)	63(6)	59(6)	6(4)	9(4)	3(5)
C(10)	−1970(5)	4125(7)	1217(6)	47(4)	72(7)	86(7)	17(4)	12(4)	6(6)
C(11)	−2161(5)	4166(7)	2441(6)	39(4)	83(7)	88(7)	19(4)	12(4)	−15(6)
C(12)	−1821(4)	3236(6)	3304(6)	25(3)	61(6)	62(6)	1(4)	9(3)	−2(5)
C(13)	−1996(5)	3218(7)	4594(6)	44(4)	93(8)	76(7)	8(4)	25(4)	−24(6)
C(14)	−1653(5)	2304(7)	5396(6)	57(4)	102(8)	62(6)	−12(5)	28(4)	−18(6)
C(15)	−1117(5)	1346(6)	4993(6)	55(4)	72(7)	64(7)	−11(4)	8(4)	1(5)
C(16)	−922(4)	1337(6)	3759(6)	38(3)	52(6)	57(6)	0(4)	8(4)	−5(5)
C(17)	−1279(4)	2278(5)	2893(5)	27(3)	48(5)	52(5)	−5(3)	8(3)	−13(5)

[a] The anisotropic temperature factor is of the form: $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + \ldots)]$.

The maximum shift in any parameter was $<0.3\sigma$. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with w = 1.0 for all the reflections. All the atomic scattering factors were taken from the International Tables for X-Ray Crystallography [14]. The computations were carried out on an RIAD-32 computer with the X-Ray Crystallographic Computing System [15]. The final atomic parameters are given in Tables I and II. A list of the observed and calculated structure factors has been deposited with the Editor.

Physical Measurements

Magnetic measurements were carried out on a polycrystalline sample with a Faraday-type magnetometer equipped with a RG-HV Cahn electrobalance. The temperature was given by a gold–iron/chromel thermocouple and read on the TC 2000 K Cryogenic Thermocouple Indicator. The applied magnetic field was 0.625 T. Independence of the magnetic susceptibility of the magnetic fields was checked at room temperature. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard [16, 17]. Corrections for diamagnetism of the dimer equal to -115×10^{-6} cm^3 mol^{-1} were calculated from Pascal's table [18, 19]. The TIP per copper ion was assumed to be 60×10^{-6} cm^3 mol^{-1}. The effective magnetic moment was calculated from the equation $\mu = 2.83\,(\chi_{Cu}T)^{1/2}$. The EPR powder spectra of the complexes were measured at room temperature on a JES-ME-3X spectrometer in the X-band, at $\nu = 9.398$ GHz.

Reflectance spectra of undiluted compound have been measured in the range 250–1000 nm on a Beckman UV 5240 spectrophotometer. Infrared spectra were recorded in KBr mulls and in nujol with a Perkin-Elmer 621 spectrophotometer in the range 400–4000 cm^{-1}.

Results and Discussion

The X-ray investigations of tetrakis(μ-crotonato)-bis(quinoline)dicopper(II) showed that the compound is a dimer in which the magnetic centres (Cu^{2+}) are coupled by four carboxylic groups of the unsaturated crotonic acid. A view of the binuclear complex is shown in Fig. 1 and of the molecular packing in Fig. 2, with marked shortened C–C van der Waals contacts.

The interatomic bond distances and angles are listed in Table III. This structure is the same as that found for the copper(II) acetate monohydrate [20, 21]. The copper atoms are coordinated by carboxylate oxygen atoms O(1), O(2)′, O(3) and O(4)′ at distances of 1.972(7), 1.976(7), 1.967(5), 1.965(4), respectively, which are typical for

TABLE II. Hydrogen Atomic Parameters (fractional $\times 10^3$).

	x	y	z	B
H(2)	252	87	312	3.3
H(3)	295	–125	171	4.0
H(6)	55	361	–199	3.7
H(7)	96	162	–364	4.0
H(9)	–132	310	–4	3.0
H(10)	–220	481	58	4.0
H(11)	–255	486	271	4.0
H(13)	–239	390	490	4.0
H(14)	–178	230	630	4.0
H(15)	–86	66	561	4.0
H(16)	–53	66	348	3.1
H(41)	435	13	321	6.0
H(42)	391	–77	418	6.0
H(43)	438	–136	303	6.0
H(81)	35	395	–462	6.0
H(82)	145	409	–400	6.0
H(83)	113	311	–517	6.0

short Cu–O bond lengths in such acetate and halogenoacetate complexes [22–26]. The four ligand atoms form a planar arrangement with the central copper atom at a distance of 0.216(5) Å from their best plane. The nitrogen atom of quinoline complexes in the square pyramidal coordination around copper has a Cu–N(1) bond length = 2.219(6) Å.

The lengths of N(1)–C(9) = 1.314(8) and N(1)–C(17) = 1.379(8) Å bonds within the quinoline ring are distinctly different. Table IV shows least-squares planes of ligands and of coordination polyhedra fragments. The crotonate ions are not planar. The dihedral angles between the four C atoms plane and the carboxyl group plane are 10.3 and 10.9°.

The copper–copper distance across the dimeric unit is 2.660(3) Å. It is dinstincly greater than 2.616(1), 2.582(1) and 2.597(1) Å in copper(II) acetate monohydrate [23] and methanol and acetic acid adducts of copper acetate [5]. It is comparable with the Cu–Cu separation = 2.663(1) Å in tetrakis-

TABLE III. Bond Lengths and Angles.

Coordination polyhedron			
Cu–Cu′	2.660(3)	N(1)–Cu–O(3)	92.5(2)
Cu–N(1)	2.219(6)	O(1)–Cu–N(1)	101.4(2)
Cu–O(1)	1.972(7)	N(1)–Cu–O(2)′	91.2(2)
Cu–O(3)	1.967(5)	O(4)′–Cu–N(1)	99.9(2)
Cu–O(2)′	1.976(7)	O(1)–Cu–O(3)	90.2(2)
Cu–O(4)′	1.965(4)	O(3)–Cu–O(2)′	87.8(2)
		O(2)′–Cu–O(4)′	90.5(2)
		O(1)–Cu–O(4)′	88.7(2)
Crotonate ions			
C(1)–O(1)	1.251(8)	O(1)–C(1)–O(2)	125.7(5)
C(1)–O(2)	1.251(7)	C(2)–C(1)–O(2)	117.6(5)
C(1)–C(2)	1.489(9)	C(2)–C(1)–O(1)	116.7(5)
C(2)–C(3)	1.305(9)	C(3)–C(2)–C(1)	122.6(6)
C(3)–C(4)	1.501(10)	C(4)–C(3)–C(2)	126.6(6)
C(5)–O(3)	1.266(8)	O(3)–C(5)–O(4)	125.3(6)
C(5)–O(4)	1.246(7)	O(4)–C(5)–C(6)	118.7(6)
C(5)–C(6)	1.491(9)	O(3)–C(5)–C(6)	116.0(5)
C(6)–C(7)	1.321(10)	C(5)–C(6)–C(7)	121.7(6)
C(7)–C(8)	1.505(12)	C(6)–C(7)–C(8)	123.9(7)
Quinoline molecule			
N(1)–C(9)	1.314(8)	Cu–N(1)–C(9)	113.1(4)
C(9)–C(10)	1.409(10)	Cu–N(1)–C(17)	128.7(4)
C(10)–C(11)	1.370(10)	C(17)–N(1)–C(9)	118.1(5)
C(11)–C(12)	1.396(9)	N(1)–C(9)–C(10)	124.1(6)
C(12)–C(13)	1.429(10)	C(9)–C(10)–C(11)	118.5(6)
C(13)–C(14)	1.348(10)	C(10)–C(11)–C(12)	119.3(7)
C(14)–C(15)	1.409(11)	C(11)–C(12)–C(17)	119.1(6)
C(15)–C(16)	1.382(9)	C(11)–C(12)–C(13)	122.3(6)
C(16)–C(17)	1.413(8)	C(17)–C(12)–C(13)	118.6(5)
C(17)–C(12)	1.418(9)	C(12)–C(13)–C(14)	120.3(7)

(continued on facing page)

TABLE III. *(continued)*

C(17)–N(1)	1.379(8)	C(13)–C(14)–C(15)	121.4(7)
		C(14)–C(15)–C(16)	120.2(6)
		C(15)–C(16)–C(17)	119.7(6)
		N(1)–C(17)–C(12)	120.8(5)
		C(12)–C(17)–C(16)	119.8(5)
		C(16)–C(17)–N(1)	119.4(5)

TABLE IV. Least-Squares Planes.

A. Displacements in Å

I	Δ	II	Δ	III	Δ	IV	Δ	V	Δ	VI	Δ
N(1)	−0.010	O(1)	−0.002	O(1)	0.0	C(1)	0.008	O(3)	0.0	C(5)	−0.026
C(9)	−0.011	O(2)′	−0.002	O(2)	0.0	C(2)	−0.007	O(4)	0.0	C(6)	0.024
C(10)	0.010	O(3)	0.002	C(1)	0.0	C(3)	−0.009	C(5)	0.0	C(7)	0.027
C(11)	0.004	O(4)′	−0.002			C(4)	0.008			C(8)	−0.026
C(12)	0.001	Cu	0.216^a								
C(13)	−0.006										
C(14)	−0.006										
C(15)	−0.001										
C(16)	0.014										
C(17)	0.005										

B. Equations of the Planes in Orthogonal Angstrom Space

I $0.7943X - 0.5350Y + 0.2877Z = 0.2999$
II $0.5276X - 0.6608Y - 0.5339Z = -1.1118$
III $-0.4076X - 0.7332Y + 0.5442Z = -0.0228$
IV $-0.4950X - 0.5920Y + 0.6360Z = -0.0259$
V $0.8343X + 0.1332Y + 0.5350Z = 0.2301$
VI $0.9160X + 0.0492Y + 0.3981Z = 0.3719$

C. Dihedral angles

Planes	Angle (°)	Planes	Angle (°)
III–IV	10.9	II–III	88.7
V–VI	10.3	II–V	86.3
		I–II	85.0

[a] Atom excluded from calculation of plane. E.s.d. for Cu displacement is 0.005 Å. E.s.d.'s for displacements of N, C and O atoms are on an average 0.009 Å.

(μ-acetato)bis(benzimidazole)dicopper(II) [27], other tetrakis(μ-acetato) complexes [28] and in several dimeric copper(II) halogenoacetates [12]. The elongation of the Cu–Cu bond was connected with the strength of an acid ligand forming the carboxylate bridge [12]. The strengths of crotonic and acetic acids are similar and the above mentioned data show that pK_a is not the only factor determining the length of the Cu–Cu binding. The elongation of Cu–Cu separation was also connected with the deviation of copper ion from the basal plane of the square pyramidal coordination polyhedra [12]. The deviation of copper ion from the CuO_4 plane is a very distinct effect, and as shown by the literature data, the Cu–basal plane distance varies from 0.190 Å for $Cu(CH_3COO)_2H_2O$ [20, 21] to 0.321 Å for $Cu(F_3COO)_2quin$ [13]. Our investigation shows that the distance in the crotonate complex (0.216 Å) is a little greater than in acetate dimer. The obtained data deny the foreseen linear relationship

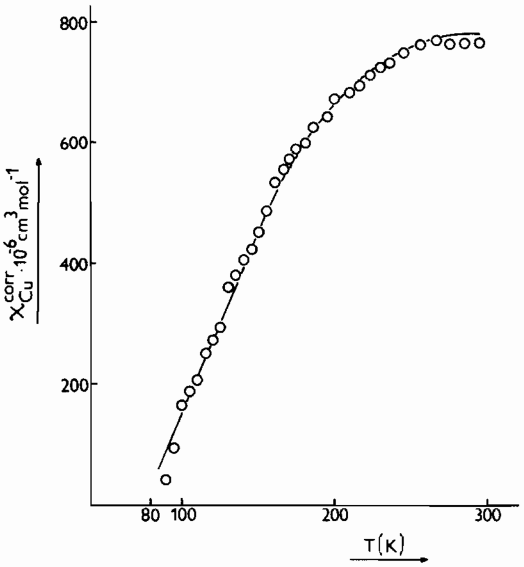

Fig. 3. Theoretical and experimental magnetic susceptibility for $Cu_2(CH_3CHCHCO_2)_4quin_2$ calculated per Cu ion. The solid line results from least-squares fitting to the theoretical Bleaney–Bowers model.

of Cu–Cu and Cu–L bond lengths [5] where L is an axial ligand.

Magnetic measurements of a polycrystalline sample of the dimer made at 80–300 °K indicated a strong temperature dependence of the magnetic susceptibility (Fig. 3). Magnetic moment decreased from 1.34 B.M. to 0.06 B.M. for 295 and 85 K, respectively. Such a temperature dependence of the magnetic moment is characteristic for copper(II) dimers with the singlet ground state (S = 0) and the energetically higher triplet state (S = 1). For determination of the singlet–triplet separation the corrected experimental magnetic susceptibilities were fit to the modified Bleaney–Bowers expression [29]:

$$\chi_{Cu}^{corr} = \frac{Ng_{av}^2\beta^2}{3kT}\,[1 + 1/3(e^{-2J/kT})]\,(1 - x) + \left(\frac{Ng_{imp}^2\beta^2}{4kT}\right)x \tag{1}$$

where χ_{Cu}^{corr} = molar magnetic susceptibility calculated per copper ion, J = exchange parameter in the Heisenberg–Dirac–Van Vleck Hamiltonian $\mathcal{H} = -2J\hat{S}_1\hat{S}_2$, x = percentage of mol of monomeric form of the complex; other symbols have their usual meaning. The spectroscopic parameter g_{av} = 2.23 obtained from the EPR spectrum was used as a constant in the process of fitting of the data. The minimization of the sum of squares of deviation

$$ERR = \sum_{i=1}^{n} (\chi_i^{calcd} - \chi_i^{exptl})^2$$

was the criterion used to determine the best fit. The singlet–triplet separation determined at ERR = 1.503×10^{-8} equals -333 cm^{-1}.

The EPR spectrum for a dimer was obtained for the polycrystalline sample X-band at room temperature. The spectrum exhibits the absorption typical for the randomly-orientated triplet state and was interpreted by means of the Hamiltonian spin

$$\mathcal{H} = g\beta HS + D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) - 2/3\ D$$

where D and E are the axial and rhombic zero field parameters respectively; other symbols have their usual meaning. Since the axial zero field parameter $|D|$ = 0.388 cm^{-1} exceeds the microwave quantum parameter $|D| > h\nu$, the EPR shows only the allowed lines, corresponding to the $\Delta M_s = \pm 1$ (H_{z1} = 538, $H_{\perp 2}$ = 4712 and H_{z2} = 5993 G). The rhombic zero-field parameter E is much lower than $|D|$ and is equal to 0.0053 cm^{-1}. The obtained compound is highly pure, as evidenced by the EPR spectrum. No lines deriving from the paramagnetic monomeric form of the complex were observed (Table V).

TABLE V. EPR Parameters.

Spectroscopic splitting factor				Zero-field splitting parameter	
$g_{\parallel}$	$g_{\perp}$	g_{av}^{a}	g_{imp}	$\lvert D\rvert$ (cm^{-1})	E (cm^{-1})
2.46	2.11	2.23	–	0.388	0.0053

[a] $g_{av}^2 = 1/3(2g_{\perp}^2 + g_{\parallel}^2)$.

The reflectance spectrum made for the dimer in the solid state presents two bands characteristic for the dimeric copper(II) carboxylates, at *ca.* 380 and 705 nm. Those so-called Bands II and I correspond to the transitions $np_{\pi} \rightarrow \delta^*(x^2 - y^2)$ combined with the Cu–OCO–Cu bridge system and to the d–d $(d_{xz}, d_{yz}) \rightarrow (d_{x^2-y^2})$ transition, respectively [30].

The authors, who examined the copper(II) carboxylates to define their structure, examined the infrared spectral range 1350–1700 cm^{-1}, in which stretching is present. In the IR spectrum of tetrakis(μ-crotonato)bis(quinoline)dicopper(II) the bands corresponding to the symmetric and asymmetric vibrations of the carboxyl bridges appear at 1417 cm^{-1} and 1596 cm^{-1} respectively.

Those bands are shifted towards higher frequencies with respect to the bands present in the IR spectrum of potassium crotonate salt (in which the carboxyl group was assumed to appear in the ionic form) by 1 and 35 cm^{-1}, respectively. From the literature data [31–34] it follows that the increase in frequency of the asymmetric and symmetric groups of the dimer against their ionic form proves that

TABLE VI. Infrared Data (cm^{-1}).

Compound	Carboxylate stretches			ν(C=C)
	ν_{asym}	ν_{sym}	$\Delta\nu$	
$Cu_2(CH_3CH{=}CHCOO)_4quin_2$	1595 vs	1417 vs	179	1660 s
$CH_3CH{=}CHCOOK$	1561 vs	1416 vs	145	1660 s

the bridging ligand is bidentate and its carboxyl group is symmetric.

The structure of tetrakis(μ-crotonato)bis(quinoline)dicopper(II) indicates that the observed considerable increase of ν_{sym}OCO frequency vibrations of dimer *versus* that of the potassium crotonate salt (35 cm^{-1}) should be considered as proof of the presence of bidentate carboxylic ligands and of the symmetric bridge groups. The symmetric ν(OCO) vibration is shifted only by 1 cm^{-1} (Table VI); similar small shifts, never greater than a few cm^{-1}, were reported by other authors [35, 36]. The relation between the shift of the ν_{sym}(OCO) vibration band and the structure of dimers has not been explicitly explained [36]. Therefore structural conclusions about the copper(II) carboxylates should be drawn carefully, based upon the positions of bands corresponding to ν_{sym}(OCO) vibrations.

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