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Solid State Structures of Nonemitting Complexes of Cuprous Iodide: (CuI(methylquinaldate))$_x$ (I), (CuI(isopropylquinaldate))$_2$ (II) and (CuI(n-butylquinaldate))$_2$ (III)

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Abstract

Cuprous iodide forms 1:1:1 complexes (Cu:I: ligand) with the methyl, isopropyl and n-butyl esters of quinaldic acid: (CuI(methylquinaldate))$_x$ (I), $CuIC_{11}H_9NO_2$, $a = 9.810(5)$, $b = 15.486(14)$, $c = 4.108(2)$ Å, $\alpha = 81.32(6)$, $\beta = 87.74(4)$, $\gamma = 108.18(5)^\circ$, $D_{calc} = 2.148$ g cm^{-3}, $Z = 2$, triclinic space group $P\bar{1}$, $R = 6.8\%$ for 2044 observed reflections; (CuI(isopropylquinaldate))$_2$ (II), $CuIC_{13}H_{13}NO_2$, $a = 9.053(4)$, $b = 22.554(10)$, $c = 10.496(3)$ Å, $\alpha = 52.37(3)$, $\beta = 115.67(3)$, $\gamma = 153.48(2)^\circ$, $D_{calc} = 1.876$ g cm^{-3}, $Z = 2$, triclinic space group $P\bar{1}$, $R = 4.7\%$ for 2279 observed reflections; (CuI(n-butylquinaldate))$_2$ (III), $CuIC_{14}H_{15}NO_2$, $a = 8.994(2)$, $b = 10.336(3)$, $c = 16.216(6)$ Å, $\beta = 101.0(2)^\circ$, $D_{calc} = 1.884$ g cm^{-3}, $Z = 4$, monoclinic space group $P2_1/c$, $R = 7.4\%$ for 1082 observed reflections.

The three complexes exhibit tetrahedral copper coordination to two iodine atoms and the carbonyl oxygen and nitrogen atoms of a single quinaldate ester molecule, however, complex **I** shows a chain of alternating copper and iodine atoms whereas **II** and **III** crystallize with rhombohedra of alternating copper and iodine atoms. These three solid materials thus display similarity to known complexes of cuprous iodide with nitrogen donor ligands in which the nitrogen atom is part of an aromatic ring system. Unlike those systems, **I**, **II** and **III** display no visible emission when excited in the UV range.

Introduction

The complexes of cuprous iodide and nitrogen donor ligands have been observed to display a wide variety of stoichiometries, structures [1, 2] and emission characteristics [3] in the solid stage. Crystalline materials have shown stoichiometries of Cu:I: ligand 1:1:0.5, 1:1:1, 1:1:1.5, 1:1:2, and 1:1:3. The solid state structures most often display the occurrence of Cu_2I_2 rhombohedra, either singly [4–6] or in combination as chairs [2], polymeric pleated sheets [7, 8], or cubes [2, 7, 9–12]. However, other structural formats which do not involve Cu_2I_2 rhombohedra are also observed, including monomers [3, 9] and chains of alternating copper and iodine atoms [2, 13]. Copper ordinarily displays tetrahedral coordination in these complexes, accepting electron pairs from nitrogen atoms of ligated organic molecules to complete its coordination sphere. Many solid state complexes of this type, when excited at wavelengths of approximately 350 nm, emit in the visible at an observed wavelength that may or may not be dependent on temperature. Others do not show observable emission.

Our interest in these complexes [12, 14, 15] focuses on families of compounds formed by CuI with identical or similar ligands which vary in stoichiometry or structural format, but also differ in emission characteristics. From observation of the structural and emission characteristics within these families, we are able to identify aspects of structure which give rise to components of the emission spectra.

Structures of the type, CuIL, in which the ligand is bidentate with hetero donor atoms, have not been studied by single crystal diffraction techniques. Thus, while the pyridine carboxylic acid derivatives offer the possibility of nitrogen, carbonyl oxygen and, in the case of the acid, carboxylic oxygen binding, the mode of complexation in the crystal has not been established. The literature contains reports of preparation of 1:1:1 complexes of CuI and the methyl, ethyl, butyl and hexyl esters of nicotinic acid [16], all of which emit, but only the hexyl ester is reported to display thermochromic emission. Structural details are unreported for these materials. Previous workers have reported two 1:1:1 complexes of CuI and methyl quinaldate (and similarly two 1:1:1 complexes each with Cl or Br replacing I) and two 1:1:1 complexes of CuI and ethylquinaldate (but only one version when Cl or Br replaces I) [17]. The two forms of the iodide complexes differ in color, a dark-brown modification and an orange–brown modification existing

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for the complex of each ester. These modifications also differ in melting point with approx. 15 °C difference reported between melting or decomposition points. Because the carbonyl stretching vibrations of the uncomplexed ester and the Cu complexed ester differ only by 5 cm^{-1} from the 1715, 1710 cm^{-1} observed in the uncomplexed methyl and ethyl quinaldate, respectively, these workers [17] suggest that the C=O group does not participate in complexation in their materials. The emission characteristics of the CuI complexes with quinaldate esters were not reported.

We have prepared a series of complexes in which L is a ligand capable of donating both oxygen and nitrogen groups to observe the effect of hetero donor and bidentate ligands upon the emission from these systems. We report here the systems; $(CuI(methylquinaldate)_x$ **(I)**, $Cu_2I_2(isopropylquinaldate)_2$ **(II)** and $Cu_2I_2(isobutylquinaldate)_2$ **(III)** which show solid state structures of types seen for nitrogen donor ligands, however, these solid state materials do not emit at room temperature or at liquid nitrogen temperature.

Syntheses

(CuI(methylquinaldate))$_x$

Quinaldic acid (1 g) was dissolved in 10 ml methanol, followed by addition of 3 ml conc. sulfuric acid, following the procedure of Mills and Hamer [18] and the resulting solution heated under reflux for 2 h. The solution was then poured into distilled water cooled to 0 °C and neutralized with solid Na_2CO_3 until effervescence ceased. The methyl ester was extracted into 30 ml of ether, from which it was isolated on evaporation of the organic solvent (melting point (m.p.) 86–87 °C) and was used without further purification.

CuI (0.15 g) and methyl quinaldate (0.147 g) (1:1 molar ratio) were dissolved in acetonitrile giving a yellow–orange solution. Purple–brown crystals of $(CuI(methylquinaldate))_x$ suitable for single crystal X-ray analysis were obtained upon slow evaporation of the solvent; decomposition 180 °C; IR 1718vs, 1620, 1595, 1505, 1460, 1433s, 1388, 1352, 1318vs, 1308vs, 1262s, 1218s, 1198s, 1160, 1142, 1118s, 1022, 981s, 955, 870, 842s, 795s, 772vs, 639, 600 cm^{-1} KBr.

Cu_2I_2(isopropylquinaldate)$_2$

The isopropyl ester of quinaldic acid was prepared by an acid catalyzed procedure as above and used as isolated. Five drops of the ester and 0.1 g of CuI (molar ratio approx. 1:1) were dissolved in 40 ml of acetonitrile, giving an orange solution. Deep red–purple crystals were obtained upon slow evaporation of the solvent; melting with decomposition 187–190 °C, color change to light orange with melting; IR 1695vs, 1613, 1593, 1505, 1463s, 1435, 1398s, 1306vs, 1300vs, 1255s, 1218, 1178s, 1125, 1110vs, 1098vs, 970, 925, 883, 852, 842, 795, 775vs, 638, 627 cm^{-1} KBr.

Cu_2I_2(n-butylquinaldate)$_2$

N-butyl quinaldate was prepared by acid catalyzed esterification of quinaldic acid with n-butanol. The crude ester was added to a solution of CuI (0.1 g) in acetontrile to give a solution of molar ratio (1:1, ester:CuI). Purple–brown crystals formed on slow evaporation of the solvent; decomposition 195–200 °C; IR 1695vs, 1618, 1590, 1503, 1458s, 1435, 1395, 1380, 1305vs, 1258s, 1217s, 1178s, 1129s, 1060, 1023, 970s, 950s, 875, 841, 795, 775vs, 737, 635, 625 cm^{-1} KBr.

Crystallographic Results

Crystals of $(CuI(methylquinaldate))_x$ (I), (CuI-(isopropylquinaldate))$_2$ (II) and (CuI(n-butylquinaldate))$_2$ (III) were mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least squares refinement of the best angular positions for fifteen independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation (λ = 0.71069 Å). Data (5611 (I), 2928 (II), 4122 (III) points) was collected at room temperature using a variable scan rate, a θ–2θ scan mode and a scan width of 1.2° below $K\alpha_1$ and 1.2° above $K\alpha_2$ to a maximum 2θ value of 60.0°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections and as the intensities of these reflections showed less that 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization and background effects. After removal of redundant and space group forbidden data (III only), observed data, (2044 (I), 2279 (II), 1082 (III) points) ($I > 3.0\sigma(I)$) was used for solution and refinement. Heavy atom positions were located using direct methods [19]. Least squares refinement [20] followed by a difference Fourier synthesis allowed location of the remainder of the nonhydrogen positions. Hydrogen atoms of the quinoline ring (I) were calculated assuming normal trigonal geometry and a C–H bond length of 0.97 Å. Hydrogen positions for **III** were determined from a difference Fourier syntheses. These positions were included in the final refinement with fixed isotropic thermal parameters but were held fixed. Anomalous dispersion corrections were made for Cu and I [21]. Scattering factors were taken from Cromer and Mann [22].

TABLE I. Crystal Data for [CuI(methylquinaldate)]$_x$ (I), [CuI(isopropylquinaldate)]$_2$ (II) and [CuI(n-butylquinaldate)]$_2$ (III)

Formula	$CuIC_{11}H_9NO_2$ (1)	$CuIC_{13}H_{13}NO_2$ (2)	$CuIC_{14}H_{15}NO_2$ (3)
M_r	377.6	405.7	419.2
a (Å)	9.810(5)	9.053(4)	8.994(2)
b (Å)	15.486(14)	22.554(10)	10.336(3)
c (Å)	4.108(2)	10.496(3)	16.216(6)
α (°)	81.32(6)	52.37(3)	90.0
β (°)	87.74(4)	115.67(3)	101.0(2)
γ (°)	108.18(5)	153.48(2)	90.0
V (Å^3)	583.7(7)	717.9(5)	1479.7(8)
F(000)	360	392	816
μMo Kα (cm^{-1})	44.76	36.46	35.40
λMo Kα (Å)	0.71069	0.71069	0.71069
D_{calc} (g cm^{-3})	2.148	1.876	1.884
Z	2	2	4
Observed reflections	2044	2279	1082
R/R_w (%)	6.8/9.3	4.7/6.3	7.4/9.8
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
G.O.F.[a]	0.38	0.38	0.32
Octants measured	$\pm h, k, \pm l$	$\pm h, k, \pm l$	$\pm h, k, l$

[a] Goodness-of-fit.

TABLE II. Positional Parameters for $CuIC_{11}H_9NO_2$ (I)

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$
Cu1	−0.7147(2)	0.2520(1)	0.7959(4)
I1	−0.5980(1)	0.2087(1)	0.3013(2)
O1	−0.6686(10)	0.4102(7)	0.5431(28)
O2	−0.7937(11)	0.4840(7)	0.2297(25)
N1	−0.9119(10)	0.2653(7)	0.7418(23)
C2	−0.9235(13)	0.3389(9)	0.5511(30)
C3	−1.0529(15)	0.3481(10)	0.4544(33)
C4	−1.1780(15)	0.2786(10)	0.5651(40)
C5	−1.1722(14)	0.1990(10)	0.7696(33)
C6	−1.2963(15)	0.1246(12)	0.8948(43)
C7	−1.2866(16)	0.0488(11)	1.0940(42)
C8	−1.1507(16)	0.0446(11)	1.1907(40)
C9	−1.0279(15)	0.1154(10)	1.0661(35)
C10	−1.0354(14)	0.1939(9)	0.8573(33)
C11	−0.7781(14)	0.4143(9)	0.4417(32)
C12	−0.6582(19)	0.5598(11)	0.1176(41)

TABLE III. Positional Parameters for $CuIC_{13}H_{13}NO_2$ (II)

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$
Cu1	0.1010(2)	0.0660(1)	−0.1560(1)
I1	0.5525(1)	0.2228(1)	−0.0150(6)
O1	0.211(1)	0.236(1)	−0.3840(6)
O2	0.435(1)	0.391(1)	−0.6682(6)
N1	0.292(1)	0.140(1)	−0.3632(7)
C1	0.326(2)	0.285(1)	−0.5134(8)
C2	0.372(2)	0.237(1)	−0.5154(8)
C3	0.495(2)	0.293(1)	−0.670(1)
C4	0.530(2)	0.244(1)	−0.663(1)
C5	0.446(2)	0.140(1)	−0.504(1)
C6	0.483(2)	0.086(1)	−0.487(1)
C7	0.419(2)	−0.007(1)	−0.328(1)
C8	0.308(2)	−0.051(1)	−0.183(1)
C9	0.259(2)	−0.007(1)	−0.192(1)
C10	0.331(2)	0.092(1)	−0.354(1)
C11	0.448(2)	0.466(1)	−0.682(1)
C12	0.795(2)	0.606(1)	−0.666(1)
C13	0.410(3)	0.514(1)	−0.859(1)

The final cycle of refinement – function minimized $\Sigma(|F_o| - |F_c|)^2$, led to final agreement factors, R = 6.8 (I), 4.7 (II), 7.4 (III) %, $R = (\Sigma||F_o| - |F_c||/\Sigma|F_o|) \times 100$. A weight equal to $1/\sigma F$ was introduced in the final cycles of refinement: R_w = 9.3 (I), 6.3 (II), 9.85 (III) %.

Positional parameters for **I**, **II** and **III** are given in Tables I, II, III and IV. The derived bond angles and distances are presented in Tables V, VI and VII respectively. Hydrogen positional parameters, anisotropic thermal parameters and listings of F_o/F_c are available, see 'Supplementary Material'.

Discussion

(Cuprous iodide(methylquinaldate))$_x$ (**I**) (Fig. 1) crystallizes with a chain of alternating copper and iodine atoms, each copper atom displaying tetrahedral coordination to two iodine atoms and the carbonyl oxygen and nitrogen atoms of a single methyl quinaldate molecule. The I–Cu–I angle is 107.84(9)° and the angle at iodine, 107.84(8)°. Copper atoms along the chain are separated by the c cell edge, 4.108 Å. The single strand or split stair polymeric combination of copper and iodine has

TABLE IV. Positional Parameters for $CuIC_{14}H_{15}NO_2$ (III)

Atom	$x(\sigma(x))$	$y(\sigma(y))$	$z(\sigma(z))$
I1	1.2004(2)	0.4268(2)	0.5917(1)
Cu1	0.9288(4)	0.3972(3)	0.5095(2)
O13	0.7826(25)	0.3546(20)	0.6055(12)
O12	0.6487(22)	0.1899(19)	0.6412(13)
N1	0.8578(25)	0.2117(18)	0.4821(13)
C2	0.7739(27)	0.1582(27)	0.5289(18)
C3	0.7168(27)	0.0287(27)	0.5178(14)
C4	0.7621(33)	−0.0428(27)	0.4580(16)
C5	0.8509(28)	0.0114(24)	0.4055(15)
C6	0.8991(25)	0.1454(23)	0.4206(15)
C7	0.9894(34)	0.1954(26)	0.3705(16)
C8	1.0288(35)	0.1355(30)	0.3041(16)
C9	0.9834(38)	0.0007(33)	0.2915(20)
C10	0.8943(30)	−0.0532(26)	0.3414(18)
C11	0.7356(29)	0.2506(31)	0.5971(19)
C14	0.6040(33)	0.2728(27)	0.7100(15)
C15	0.5255(33)	0.1860(30)	0.7618(19)
C16	0.4709(29)	0.2618(36)	0.8318(21)
C17	0.4118(41)	0.1788(36)	0.8871(23)

TABLE V. Bond Angles (°) and Distances (Å) for $CuIC_{11}H_9NO_2$ (I)

Cu1–I1	2.568(2)	Cu1–I1–Cu1′	107.84(8)
Cu1–I1′	2.514(2)	I1–Cu1–I1′	107.84(9)
I1–Cu1′	2.514(2)	I1–Cu1–O1	94.9(3)
Cu1–O1	2.40(1)	I1′–Cu1–O1	121.9(3)
Cu1–N1	2.02(1)	I1–Cu1–N1	115.9(3)
N1–C2	1.32(2)	I1′–Cu1–N1	131.5(3)
C2–C3	1.39(2)	N1–Cu1–O1	74.9(4)
C3–C4	1.36(2)	Cu1–N1–C2	119.6(7)
C4–C5	1.40(2)	Cu1–N1–C10	121.5(9)
C5–C6	1.40(2)	N1–C2–C3	124.0(1)
C5–C10	1.43(2)	C2–C3–C4	119.0(1)
C6–C7	1.36(2)	C3–C4–C5	119.0(1)
C7–C8	1.42(2)	C4–C5–C6	112.0(1)
C8–C9	1.37(2)	C4–C5–C10	143.0(9)
C9–C10	1.40(2)	C5–C6–C7	121.0(1)
C10–N1	1.37(1)	C6–C7–C8	121.0(1)
C2–C11	1.53(2)	C7–C8–C9	120.0(1)
C11–O1	1.18(2)	C8–C9–C10	121.0(1)
C11–O2	1.33(2)	C9–C10–C5	119.0(1)
O2–C12	1.47(2)	C9–C10–N1	120.0(1)
		C10–C5–C6	119.0(1)
		C10–N1–C2	118.0(1)
		N1–C10–C5	121.0(1)
		N1–C2–C11	113.0(1)
		C2–C11–O1	123.0(1)
		C2–C11–O2	111.0(1)
		O1–C11–O2	126.0(1)
		C11–C2–C3	123.0(1)
		C11–O2–C12	114.0(1)
		C11–O1–Cu1	106.0(8)

been previously observed for (CuIacridine)$_x$ [2] and for (CuIcollidine)$_x$ [13], both of which show three coordinate copper presumably due to the steric

TABLE VI. Bond Angles (°) and Distances (Å) for $CuIC_{13}H_{13}NO_2$ (II)

Cu1–I1	2.585(3)	I1′–Cu1–I1	120.9(2)
Cu1–Cu1′	2.544(2)	I1–Cu1–O1	101.4(2)
Cu1–N1	2.04(1)	I1–Cu1–N1	115.5(2)
Cu1–O1	2.33(1)	O1–Cu1–N1	76.6(6)
N1–C2	1.33(1)	O1–Cu1–I1′	112.0(3)
N1–C10	1.36(3)	N1–Cu1–I1′	118.8(2)
C2–CI	1.48(3)	Cu1–I1–Cu1′	59.1(1)
C2–C3	1.42(2)	Cu1–N1–C10	123.8(5)
C3–C4	1.37(4)	Cu1–N1–C2	117.6(15)
C4–C5	1.41(2)	Cu1–O1–C1	107.4(15)
C5–C10	1.43(2)	N1–C10–C5	121.3(11)
C5–C6	1.41(4)	N1–C10–C9	118.8(14)
C6–C7	1.38(2)	N1–C2–C3	123.8(20)
C7–C8	1.41(3)	N1–C2–C1	114.8(13)
C8–C9	1.37(4)	C2–C3–C4	118.2(12)
C9–C10	1.42(2)	C3–C4–C5	119.8(15)
C1–O1	1.21(2)	C4–C5–C10	118.3(21)
C1–O2	1.32(1)	C4–C5–C6	122.6(16)
O2–C11	1.48(3)	C6–C5–C10	119.0(11)
C11–C12	1.52(1)	C5–C6–C7	120.4(18)
C11–C13	1.55(2)	C6–C7–C8	119.5(25)
		C7–C8–C9	122.5(13)
		C8–C9–C10	118.6(14)
		C9–C10–C5	119.9(19)
		C1–C2–C3	121.3(12)
		O1–C1–C2	123.5(12)
		O1–C1–O2	124.4(21)
		C2–C1–O2	112.1(13)
		C1–O2–C11	91.0(8)
		O2–C11–C12	107.5(17)
		O2–C11–C13	104.1(16)
		C12–C11–C13	113.8(8)

TABLE VII. Bond Angles (°) and Distances (Å) for [CuI(n-butylquinaldate)]$_2$ (III)

Cu1–I1	2.56(8)	Cu1–I1–Cu1′	58.9(1)
Cu1–I1′	2.57(5)	I1–Cu1–I1′	121.0(1)
Cu1–I1′	2.52(1)	I1–Cu1–O13	106.6(5)
Cu1–N1	2.04(2)	I1′–Cu1–O13	108.9(5)
Cu1–O13	2.26(6)	I1–Cu1–N1	116.8(6)
N1–C2	1.29(5)	I1′–Cu1–N1	116.1(6)
C2–C3	1.43(4)	N1–Cu1–O13	76.5(8)
C2–C11	1.54(4)	Cu1–N1–C2	117(2)
C3–C4	1.34(4)	Cu1–N1–C6	122(2)
C4–C5	1.39(5)	C2–N1–C6	120(2)
C5–C6	1.45(3)	N1–C2–C3	124(3)
C5–C10	1.35(4)	N1–C2–C11	112(2)
C6–N1	1.32(4)	C11–C2–C3	122(2)
C6–C7	1.35(5)	C2–C3–C4	117(2)
C7–C8	1.34(5)	C3–C4–C5	120(3)
C8–C9	1.45(5)	C4–C5–C6	117(2)
C9–C10	1.36(6)	C10–C5–C6	118(2)
C11–O12	1.31(5)	C10–C5–C4	123(2)
C11–O13	1.15(4)	N1–C6–C7	122(2)
O12–C14	1.52(4)	C5–C6–C7	117(2)
C14–C15	1.49(5)	C5–C6–N1	120(2)

(continued)

TABLE VII. *(continued)*

C15–C16	1.53(5)	C6–C7–C8	125(3)
C16–C17	1.41(6)	C7–C8–C9	116(3)
		C8–C9–C10	119(3)
		C9–C10–C5	122(3)
		C2–C11–O13	122(3)
		C2–C11–O12	109(2)
		O13–C11–O12	128(3)
		C11–O12–C14	113(2)
		O12–C14–C15	107(2)
		C14–C15–C16	111(3)
		C15–C16–C17	111(3)

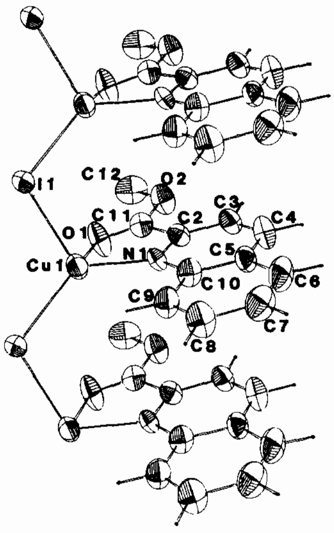

Fig. 1. Projection view of [CuI(methylquinaldate)]$_x$ (I).

demands of pyridine with methyl groups at both *ortho* positions. The steric demands of diortho-substituents have been observed to lead to three coordinate copper in the (CuI(2,6-dimethylpyridine))$_2$ rhombohedron [13] as well.

The structures of CuI and quinaldic esters in which substitution at the *ortho* positions of the pyridine ring provides a second ligation site and limits further Cu binding to a maximum of two iodine atoms, thus could not display chair, pleated sheet polymer or cube forms. Single strand polymeric or rhombic forms are observed.

Structure **I** displays similarities to (CuIacridine)$_x$ and (CuIcollidine)$_x$ despite the differences in coordination number for copper. These similarities include: Cu–I distances; 2.514(2), 2.549(2), 2.543(9) Å; Cu–N distances 2.02(1), 1.990(7), 2.01(2) Å; I–Cu–I angles, 107.84(9), 107.70(5), 109.7(1)°; and Cu–I–Cu angles, 107.84(8), 107.70(5), 109.7(1)° respectively.

CuI distances for these three single strand polymers average 2.535 Å, shorter than those normally observed in CuIligand cubes and polymeric pleated sheets where each Cu atom has three iodine neighbors (av. 2.698(3) [12] and 2.706(3) Å [8] respectively) but longer than those observed (2.388(2) Å [23]) in CuI_2^- where copper has only two neighbors (both iodine) and presumably exhibits multiple bond character.

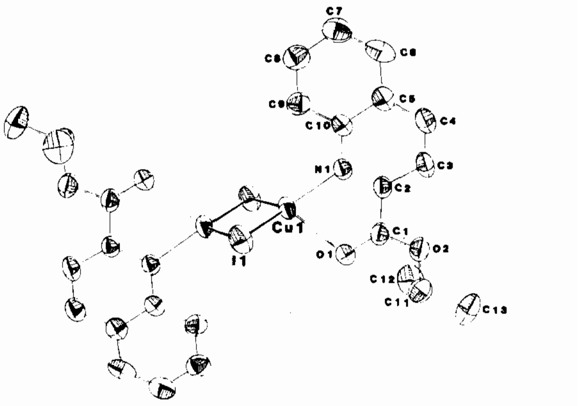

Fig. 2. Projection view of [CuI(isopropylquinaldate)]$_2$ (II).

(CuIisopropylquinaldate)$_2$ (**II**) (Fig. 2) and (CuI(n-butylquinaldate))$_2$ (**III**) (Fig. 3) crystallize with planar rhombohedra of alternating copper and iodine atoms (Cu–I 2.585(3) (**II**), 2.57(8) (**III**) Å; I–Cu–I′ 120.9(2)° (**II**), 121.0(1)° (**III**); Cu–I–Cu′ 59.1(1)° (**II**), 58.9(1)° (**III**)) to which are bound two molecules of alkylquinaldate via coordination of the carbonyl oxygen (Cu–O 2.33(1) (**II**), 2.26(6) (**III**) Å) and nitrogen atoms (Cu–N 2.04(1) (**II**), 2.04(2) (**III**) Å) of a single organic molecule to each copper atom. The planes of the quinoline rings (standard deviation (s.d.) 0.02 (**II**), 0.02 (**III**)) are nearly perpendicular to the planes of the Cu_2I_2 rhombs, subtending angles of 85.8° (**II**) and 88.6° (**III**) to those planes. The carbonyl groups (C, C, O, O s.d. 0.05 (**II**), 0.005 (**III**)) are close to coplanar with the quinoline rings (interplanar angle 7.38° (**II**), 1.26° (**III**)) and thus resonance delocalization of electron density over the ten-membered ring and the conjugated carbonyl group is possible. Similarly in **I**, the atoms of the quinoline ring (s.d. 0.01) subtend an angle of 4.96° with the plane of the atoms (C, C, O, O) of the ester group (s.d. 0.006). Carbonyl bonds are 1.18(2), 1.21(2) (**II**) and 1.15(4) (**III**) Å as compared to normal C=O bond lengths of 1.23(1) [24] for esters indicating little delocalization of the normal electron density from this carbonyl bond. Thus structures **I**, **II** and **III** all show coordination of the carbonyl oxygen to copper without any significant change in the electron density of the carbonyl bond. This view is reinforced by the observation of the C=O stretching band in complexed and uncomplexed methyl quinaldate at similar positions 1718 (**I**) and 1715 cm^{-1} respectively.

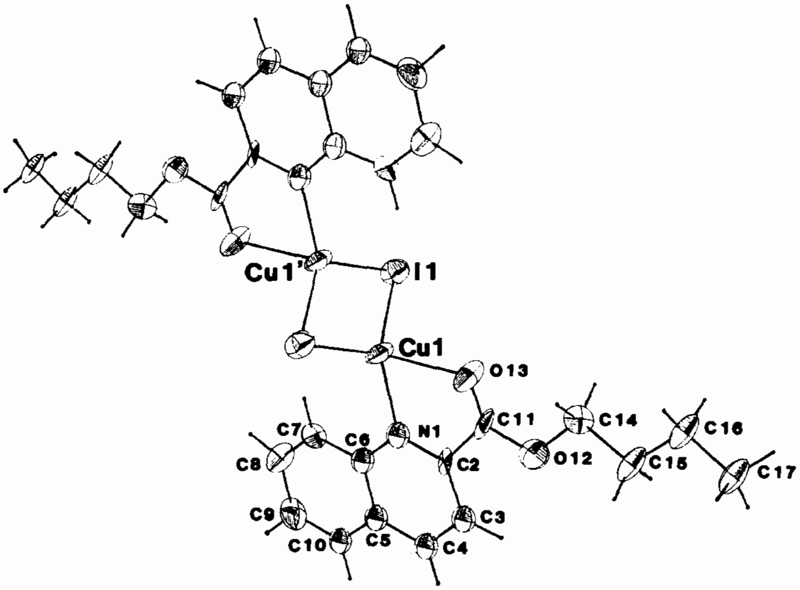

Fig. 3. Projection view of [CuI(n-butylquinaldate)]$_2$ (III).

Nevertheless, the Cu–O distance represents an interactive distance. Similar Cu–carbonyl oxygen distances in the complex of bis(10-methylisoalloxazine) [25] with copper(I) are 2.27(2) and 2.21(2) Å. In this complex a similar (–Cu–N=C–C=O–) five-membered ring is observed with both N and carbonyl oxygen involvement with Cu(I). (Copper–nitrogen distances are 1.94(2) and 1.92(2) Å). The structure of cuprous acetate [26] shows copper atoms bridged in pairs by acetate groups (Cu–O, 1.89(2), 1.90(2) Å) but with a Cu–O distance of 2.31(2) Å to a neighboring acetate oxygen atom.

Copper iodide rhombic structures such as **II** and **III** are common in the literature of CuI nitrogen donor ligand structures. Cu–Cu distances observed range from 2.535(9) to 3.576(2) Å. Thus these structures display flexible Cu–I–Cu angles and the ability to change the proximity of copper atoms in response to structural parameters which are not entirely obvious. It appears that ligands of smaller bulk permit opening of the I–Cu–I angle and thus closer Cu–Cu involvement. Thus 2,9-dimethylphenanthroline (Cu•••Cu 3.083(3); pyridine (Cu•••Cu, 2.699(5) Å in complexes of type Cu:ligand, 1:2 and 2,6-dimethylpyridine (Cu:ligand, 1:1 with tricoordinate copper) (Cu•••Cu, 2.586(5) Å) form a series of decreasing ligand bulk at copper and Cu•••Cu distances decrease with the decreasing bulk. Less obvious is the reason for the copper–copper separation of 3.364(5) Å observed in Cu_2I_2-quinaldate$_4$ but 2.866(3) Å observed in Cu_2I_2-quinoline$_4$•quinoline and 3.137(2) Å in Cu_2I_2-quinoline$_4$•CH_3CN. The inclusion of a molecule of quinoline or acetonitrile in the unit cell causes changes in Cu•••Cu proximity. Structures **II** and **III** (Cu•••Cu 2.544(2) (**II**) and 2.53(1) (**III**) Å display close Cu•••Cu distances compared to others observed in Cu_2I_2 rhombohedra.

Previous studies of emission from solid state CuILigand systems have led to the tentative identification of three structural features identified with components of the emission spectra: (a) Cu•••Cu distances of less than 2.7 Å which give rise to intercopper $d_{10} \rightarrow d^9s^1$ excitation and corresponding emission; (b) Cu bonding to aromatic ring systems which permits $d^{10} \rightarrow \pi^*$ excitation (metal to ligand charge transfer) and thus emission; and (c) interligand $\pi \rightarrow \pi^*$ excitation which has been observed when aromatic ligands are packed in parallel planes and separated by 3.325(12), 3.279(19) Å, a separation which is apparently decreased on cooling to an interactive one, resulting in the emission spectrum of the ligand alone, slightly shifted in wavelength from that arising from the noncomplexed ligand. Complex **I**, with a metal–metal separation of 4.108(2) Å is not a candidate for emission due to the first of these phenomena but might be expected to demonstrate visible evidence of b and c types of excitation. Complexes **II** and **III**, without suitable packing of aromatic ligands might be expected to display evidence of excitation of types a and b. However the energy levels of the aromatic rings of the quinoline molecule would be expected to be changed by the effects of the electron withdrawing ester groups and thus the energy levels of the aromatic ring are somehow altered to make this excitation of greater energy or to make other, radiationless, decay mechanisms more efficient. Thus interligand transitions and metal to ligand charge transfer mechanisms are somehow unfavorable or do not result in visible emission. The lack of evidence of metal to metal interaction is apparently due to alteration of the metal energy levels by the coordination to oxygen. This view is supported by the observation of emission from systems of nicotinic acid derivatives in which an alkyl carboxylate is substituted on the pyridine ring, but in a position *meta* to the coordinating nitrogen atom and the carbonyl oxygen is not coordinated. In these systems the overall deactivation of the aromatic ring must be similar although resonance effects on the basicity of the nitrogen atom differ with *ortho* and *meta* substitution. Further work will focus on elucidation of these differences.

Supplementary Material

Hydrogen positional parameters, anisotropic thermal parameters and F_o/F_c listings are available from the authors on request.

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