Supplementary Material (ESI) for Chemical Communications

Tetranuclear copper(I) clusters: Impact of bridging carboxylate ligands on solid state structures and photoluminescence

Yulia Sevryugina, Oleksandr Hietsoi, and Marina A. Petrukhina*

Department of Chemistry, University at Albany, State University of New York, 1400 Washington Avenue, Albany, New York 12222, USA

SUPPLEMENTARY INFORMATION

Experimental details

General procedures

All synthetic reactions and manipulations were carried out under a dry dinitrogen atmosphere using standard Schlenk and vacuum-line techniques. Sublimation–deposition procedures were performed in small glass ampules (*ca.* 7 cm long with an O.D. of 1.1 cm), which were sealed under vacuum (*ca*. 10^{-2} Torr) and then placed in electric furnaces having a small temperature gradient along the length of the tube.

Starting materials

The title compounds were prepared by a ligand exchange procedure starting with unligated copper(I) trifluoroacetate that was synthesized according to the literature method.[1] Anhydrous benzene was purchased from Aldrich. 3-Fluorobenzoic, (3-F)C_6H_4COOH; 2,3,4-trifluorobenzoic, (2,3,4-F)$_3C_6H_2COOH$; and pentafluorobenzoic, C_6F_5COOH, acids were purchased from SynQuest Fluorochemicals and used as received.

Physical measurements

The infrared spectra were obtained using KBr pellets on a Nicolet Magna 550 FTIR spectrometer. The photoluminescence spectra were collected on a Varian Cary Eclipse spectrophotometer in the 250–750 nm range at room temperature. The PMT detector was positioned at 90º to the incident beam and the default settings (slits widths 5 nm and integration time 0.5 s) were applied. Bulk single crystalline samples were placed in a Varian Cary Sub-micro Fluorometer cell, which was mounted in a standard single cell holder with base. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Canada.

Syntheses

$[Cu(O_2C(3\text{-}F)C_6H_4)]$ (1). $[Cu_4(O_2CCF_3)_4]$ (0.797 g, 1.13 mmol) and $(3\text{-}F)C_6H_4COOH$ (0.945 g, 6.75 mmol) were loaded in a Schlenk flask inside a glove box and 55 mL of benzene were added to the mixture. A homogeneous light blue solution was refluxed overnight and then evaporated to dryness to afford a very pale blue solid. It was heated at 90–100 °C under vacuum for several days to remove the excess of unreacted acid. Yield 0.594 g, 65%. Air-stable colorless blocks of **1** were obtained by sublimation–deposition of the crude powder at 220 °C in one week. Found: C, 41.57; H, 1.74. Calc. for $C_{28}H_{16}Cu_4F_4O_8$: C, 41.48; H, 1.98%. PL (250–750 nm, λ_{ex} = 350 nm, solid, λ_{max}, nm) 502. IR (KBr, ν_{max}/cm^{-1}): 3080w, 1598sh, 1557s, 1485m, 1443s, 1402s, 1308sh, 1266m, 1226s, 1155w, 1100w, 1074w, 1003w, 929m, 888m, 797s, 754s, 680m, 671m, 554m, 531m, 518sh.

$[Cu(O_2C(2,3,4\text{-}F)_3C_6H_2)]$ (2). The title compound was prepared by a procedure similar to that for **1** using $[Cu_4(O_2CCF_3)_4]$ (0.321 g, 0.45 mmol) and $(2,3,4\text{-}F)_3C_6H_2COOH$ (0.582 g, 3.31 mmol). An overnight reflux in benzene (40 mL) followed by solvent removal *in vacuo* afforded a very pale blue powder. It was heated at 90–100 °C under vacuum for several days to remove the excess of unreacted acid. Yield 0.347 g, 80%. Air-stable colorless blocks of **2** were obtained by sublimation–deposition of the crude powder at 160–220 °C for 4–12 days. Found: C, 35.48; H, 0.75; O, 12.95. Calc. for $C_{28}H_8Cu_4F_{12}O_8$: C, 35.21; H, 0.84; O, 13.01%. PL (250–750 nm, λ_{ex} = 350 nm, solid, λ_{max}, nm) 507. IR (KBr, ν_{max}/cm^{-1}): 3124w, 3104w, 1640sh, 1621m, 1603m, 1568s, 1506m, 1472m, 1407s, 1315m, 1285m, 1253w, 1227w, 1148w, 1046m, 951m, 834m, 807m, 773s, 752m, 708m, 648m.

$[Cu(O_2CCF_3)_{1/2}(O_2CC_6F_5)_{1/2}]$ (3). $[Cu_4(O_2CCF_3)_4]$ (0.900 g, 1.27 mmol) and C_6F_5COOH (0.526 g, 2.48 mmol) were loaded in a Schlenk flask inside a glove box and the mixture was dissolved in toluene (50 mL). The homogeneous light green solution was refluxed overnight and then evaporated to dryness to afford a green oily solid. It was heated at 90–105 °C under vacuum for several days to remove the excess of unreacted acid. Yield 0.336 g, 50%. Crystals of **3** as colorless blocks were obtained by sublimation-deposition of the crude powder at 150 °C in four days. Found: C, 23.63; O, 14.13. Calc. for $C_{18}Cu_4F_{16}O_8$: C, 23.96; O, 14.38%. PL (250–750 nm, λ_{ex} = 350 nm, solid, λ_{max}, nm) 583. IR (KBr, ν_{max}/cm^{-1}): 3219w, 3092w, 2973w, 2853w, 1676m, 1658sh, 1653s, 1633s, 1609s, 1584m, 1573sh, 1560m, 1527m, 1496s, 1490sh, 1475m, 1427s, 1417m, 1409s, 1396sh, 1379m, 1302w, 1204s, 1156m, 1117m, 996s, 860w, 762m, 734m. ^{19}F NMR (acetone, 22 °C): δ −68.6, −132.8, −145.4, −151.9.

$[Cu(O_2CC_6F_5)]$ (6). $[Cu_4(O_2CCF_3)_4]$ (0.450 g, 0.64 mmol) and C_6F_5COOH (0.810 g, 3.81 mmol) were loaded in a Schlenk flask inside a glove box and the mixture was dissolved in benzene (60 mL). The homogeneous light blue solution was refluxed overnight and then evaporated to dryness to afford a light blue powder. It was heated at *ca*. 70 °C under vacuum for several days to remove the excess of unreacted acid. Yield *ca*. 30%. Crystals of **6** as very thin colorless needles, non-suitable for X-ray analysis, were obtained by sublimation of the crude powder at 132 °C in five days. Found: C, 30.34; O, 12.13. Calc. for $C_7CuF_5O_2$: C, 30.62; O, 11.95 %. PL (250–750 nm, λ_{ex} = 350 nm, solid, λ_{max}, nm) 589. IR (KBr, ν_{max}/cm^{-1}): 1672s, 1645s, 1633s, 1574s, 1526s, 1494s, 1473m, 1426s, 1407s, 1376sh, 1290sh, 1201s, 1164s, 1118m, 1081m, 1038w, 996s, 948m, 861m, 839m, 817w, 807w, 785m, 769m, 732m. ^{19}F NMR (acetone, 22 °C): δ −132.8, −145.6, −151.9.

X-ray crystallographic procedures

The X-ray intensity data were measured at 173(2) K (Bruker CRYOFLEX) on a Bruker SMART APEX CCD-based X-ray diffractometer system equipped with a Mo-target X-ray tube (λ = 0.71073 Å) operated at 1800 W power. The crystals were mounted on a goniometer head with silicone grease. A total of 1850 frames were collected with a scan width of 0.3° in ω and an exposure time of 20 s/frame for each experiment. The frames were integrated with the Bruker SAINT software package[2] using a narrow-frame integration algorithm. The final cell constants were based upon the refinement of the XYZ-centroids of several thousands reflections above 20σ(I). Analysis of the data showed negligible decay during data collection. The data were corrected for absorption effects using the empirical method (SADABS).[3] The structures were solved and refined using the Bruker SHELXTL (Version 6.1) software package.[4]

Crystallographic data and X-ray experimental conditions for **1**–**3** are listed in Table 1. All non-hydrogen atoms in **1**–**3** were refined anisotropically, except for the carbon and fluorine atoms of four disordered groups in **3**, for which the disorder was modeled over three rotational orientations. All hydrogen atoms in **1** were included at idealized positions for structure factor calculations. All hydrogen atoms in **2** were found in the difference Fourier map and refined independently.

Compound **1** crystallizes in the monoclinic space group $C2/c$ (Z = 4) and has a two-fold rotation axis at the center of the Cu_4-core. Compound **2** crystallizes in the orthorhombic space group $Fddd$ (Z = 8). Crystallographically independent are two Cu-atoms, which reside on a two-fold axis, and one carboxylate ligand. The rest of atoms in **2** is generated by three two-fold axes running parallel to the unit cell axes a, b, and c. Compound **3** crystallizes in the triclinic space group $P\bar{1}$ (Z = 4) and contains two crystallographically independent tetramers in the asymmetric

unit, which are similar but not identical. In contrast to C_1 symmetry of molecule **3**, the point symmetry of molecules **1** and **2** is C_{2v}.

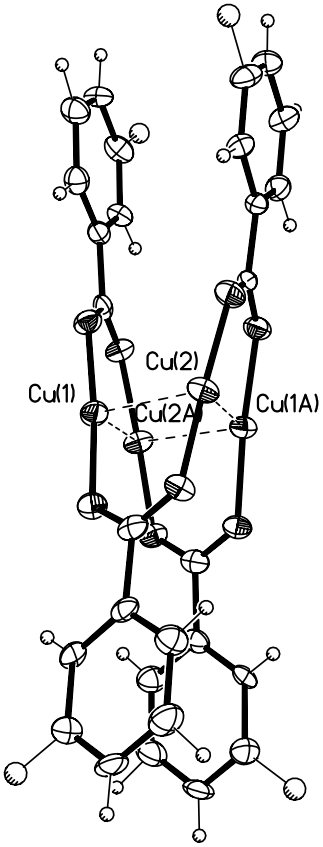

Fig. 1 A perspective drawing of the $[Cu_4(O_2C(3\text{-}F)C_6H_4)_4]$ (**1**) molecule with the Cu(I) core shown by dashed lines. Atoms are represented by thermal ellipsoids at the 45% probability level. Letter "A" in the atom labels indicates that these atoms are at equivalent position (-x, y, 3/2-z).

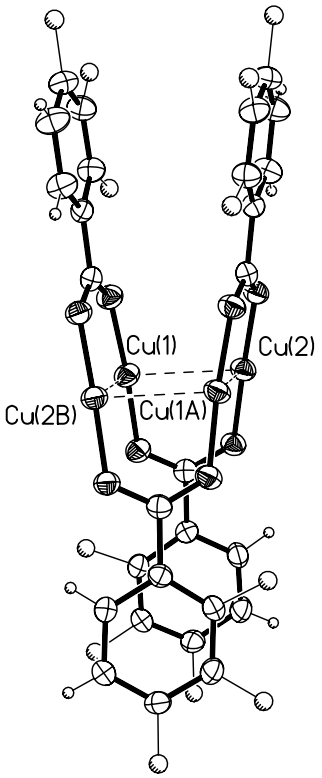

Fig. 2 A perspective drawing of the $[Cu_4(O_2C(2,3,4\text{-}F)_3C_6H_2)_4]$ (**2**) molecule with the Cu(I) core shown by dashed lines. Atoms are represented by thermal ellipsoids at the 45% probability level. Letter "A" in the atom label indicates that atom is at equivalent position (5/4-x, 1/4-y, z). Letter "B" in the atom label indicates that atom is at equivalent position (5/4-x, y, 1/4-z).

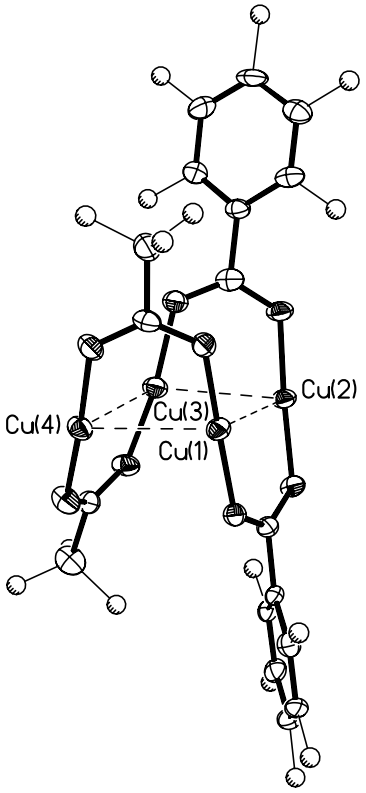

Fig. 3 A perspective drawing of the $[Cu_4(O_2CCF_3)_2(O_2CC_6F_5)_2]$ (**3**) molecule with the Cu(I) core shown by dashed lines. Atoms are represented by thermal ellipsoids at the 45% probability level. Only one of two crystallographically independent Cu_4-tetramers is shown.

Table 1. Crystallographic data and structural refinement for $[Cu_4(O_2C(3\text{-}F)C_6H_4)_4]$ (**1**), $[Cu_4(O_2C(2,3,4\text{-}F)_3C_6H_2)_4]$ (**2**), and $[Cu_4(O_2CCF_3)_2(O_2CC_6F_5)_2]$ (**3**).

	1	**2**	**3**
formula	$C_{28}H_{16}Cu_4F_4O_8$	$C_{28}H_8Cu_4F_{12}O_8$	$C_{18}Cu_4F_{16}O_8$
fw	810.57	954.50	902.34
crystal description	colorless block	colorless block	colorless block
crystal size (mm^3)	0.05 × 0.05 × 0.04	0.10 × 0.07 × 0.06	0.06 × 0.05 × 0.04
T (K)	173(2)	173(2)	173(2)
crystal system	monoclinic	orthorhombic	triclinic

space group	*C*2/*c*	*Fddd*	$P\bar{1}$
a (Å)	17.1591(18)	15.7443(19)	11.4301(8)
b (Å)	16.0078(16)	16.574(2)	14.4443(11)
c (Å)	12.3894(13)	21.682(3)	16.7589(12)
α (º)			71.969(1)
β (º)	129.578(1)		74.374(1)
γ (º)			70.565(1)
V (Å^3)	2623.0(5)	5658.1(12)	2438.0(3)
Z	4	8	4
λ (Å)	0.71073	0.71073	0.71073
D_{calc} (g cm^{-3})	2.053	2.241	2.458
μ (mm^{-1})	3.281	3.100	3.611
transmission factors	0.8531 – 0.8799	0.7468 – 0.8358	0.8125 – 0.8690
θ_{max}	24.99	28.21	28.39
unique data	2302	1706	10984
observed data [$I > 2\sigma(I)$]	1535	1313	6917
parameters refined	199	127	865
quality-of-fit[a] on F^2	1.061	1.015	0.961
$R1$[b], $wR2$[c] [$I > 2\sigma(I)$]	0.0538, 0.1162	0.0390, 0.0967	0.0538, 0.1062
$R1$[b], $wR2$[c] (all data)	0.0933, 0.1321	0.0542, 0.1074	0.0992, 0.1241
$\Delta\rho_{max, min}$ (e A^{-3})	0.852, –0.484	1.164, –0.453	0.905, –0.734

[a] Quality-of-fit = $[\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{params})]^{1/2}$.
[b] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[c] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (º) for the $[Cu_4(O_2CR)_4]$ complexes **1**–**5**.

R =	C_6H_5	(3-F)C_6H_4	(2,3,4-F)$_3C_6H_2$	CF_3	CF_3/C_6F_5
	4[b, 5]	**1**	**2**	**5**[1]	**3**[b]
Cu···Cu$_{carb-bridged}$	2.742(6)/2.719(4) 2.720(6)/2.753(6) 2.709(6)/2.732(6) 2.756(7)/2.770(5)	2.7280(11) 2.7120(12)	2.6895(6)	2.759(1) 2.719(1) 2.819(1) 2.833(1)	2.7483(10)/2.7247(11) 2.799(1)/2.8122(10) 2.8319(10)/2.8142(10) 2.8093(10)/2.7721(11)
Cu···Cu$_{non-bridged}$	3.180(5)/2.968(6) 4.442(6)/4.615(6)	2.8790(16) 4.6142(17)	2.9274(11) 4.5127(11)	2.975(1) 4.700(1)	2.7577(11)/2.8158(11) 4.8616(10)/4.7831(10)
Cu–O$_{carb}$[a]	1.840(15)	1.857(4)	1.8528(19)	1.870(5)	1.873(4)
Cu···O				2.621(6)	2.523(4)/2.610(4) 2.740(4)/2.745(4) 2.511(4)/2.405(4)
Cu–Cu–Cu	71.4(2)/66.0(1) 108.8(2)/114.0(2) 71.0(2)/65.0(1) 108.8(2)/115.0(2)	63.91(3) 116.03(3)	65.94(2) 114.06(2)	64.46(4) 118.21(4) 64.78(4) 112.52(4)	59.61(3)/61.11(3) 120.19(4)/119.43(4) 58.53(3)/60.53(3) 121.19(4)/117.85(4)

[a] Averaged. [b] Two crystallographically independent units.

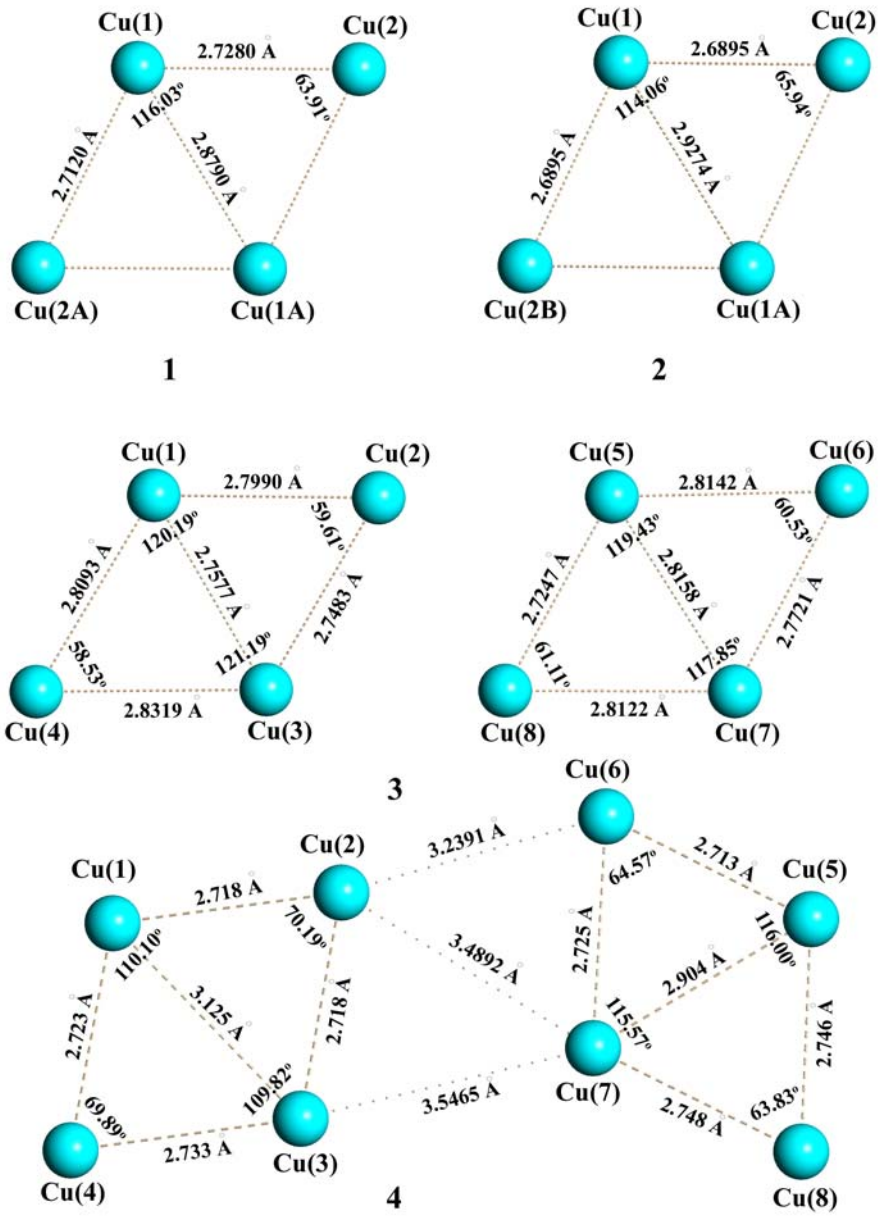

Fig. 4 The Cu_4-core structures in **1**, **2**, **3** (two crystallographically independent units) and **4**. Letters "A" or "B" in the atom labels indicate that these atoms are at equivalent positions.

Details of solid-state packing

A thorough analysis of the solid state packing of the $[Cu_4(O_2CR)_4]$ molecules, R = (3-F)C_6H_4 (**1**), (2,3,4-F)$_3C_6H_2$ (**2**), and $(CF_3)/(C_6F_5)$ (**3**), revealed intramolecular π–π stacking

interactions of 4.16 and 3.80 Å in **1** with dihedral angles between the C_6FH_4-planes of 13.2 and 4.6º, respectively, 4.11 Å in **2** (dihedral angle between the $C_6F_3H_2$-planes of 12.6º), 4.24 and 4.36 Å in 3 (dihedral angles between the C_6F_5-planes of 13.4º and 6.6º).

The closest H···F interactions in **1** fall in the 2.53–2.73 Å range with the C–H···F angles varying from 117 to 170º. The analogous contacts in **2** are 2.49–2.83 Å (C–H···F angles in the 129–157º range), respectively. However, one should keep in mind that the hydrogen atoms are fixed at idealized positions in the crystal structure of **1**.

Photoluminescence.

It should be noted here that that all carboxylic acids used to prepare copper(I) carboxylates **1**–**3** show no emission upon excitation at 350 nm at room temperature, at which copper(I) complexes **1**–**3** emit in the range of 502–583 nm. However, these carboxylic acids are luminescent upon excitation at λ_{ex} = 290 nm in the solid state, displaying emissions at 372 and 704 nm for (3-F)C_6H_4COOH; 313, 363, and 621 nm for (2,3,4-F)$_3C_6H_3$COOH; and 344 and 670 nm for C_6F_5COOH. Trifluoroacetic acid, CF_3COOH, which is liquid at ambient conditions, displays a broad emission band centered at *ca*. 369 nm (λ_{ex} = 280 nm).

References

[1] F. A. Cotton, E. V. Dikarev and M. A. Petrukhina, *Inorg. Chem*., 2000, 39, 6072.
[2] *SAINT*, *Version 6.02*; Bruker AXS, Madison, WI, 2001
[3] *SADABS*; Bruker AXS, Inc.: Madison, WI, 2001.
[4] *SHELXTL*, *Version 6.10*; Bruker AXS Inc.: Madison, WI, 2001.
[5] M. G. B. Drew, D. A. Edwards and R. Richards, *J. Chem. Soc. Dalton Trans*., 1977, 299.