Tetranuclear copper(I) clusters: impact of bridging carboxylate ligands on solid state structure and photoluminescence†

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Received (in Austin, TX, USA) 25th May 2007, Accepted 28th June 2007
First published as an Advance Article on the web 18th July 2007
DOI: 10.1039/b707957e

The X-ray crystallographic characterization and solid state photoluminescence (PL) study of three new tetranuclear copper(I) clusters, $[Cu_4(O_2CR)_4]$, R = (3-F)C_6H_4 (1), (2,3,4-F)$_3C_6H_2$ (2), and CF_3/C_6F_5 (3), revealed a dependence of PL on the structural type.

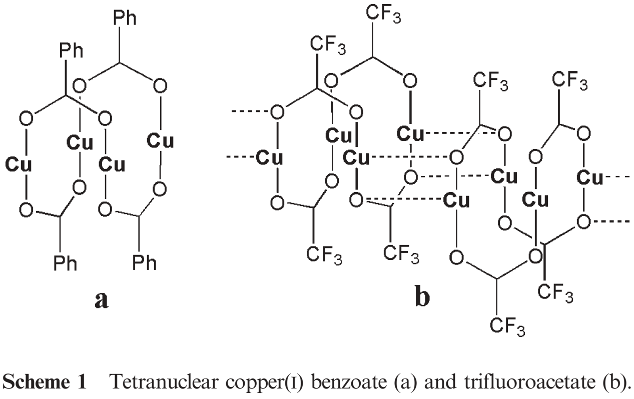
Polynuclear complexes of copper(I), silver(I), and gold(I) attract considerable interest due to their remarkable photophysical properties[1] and are broadly studied as potential optoelectronic materials.[2] The attractive interactions between closed d^{10} shells in various clusters are subjects of special attention[3] since the arrangement of metal centers and, in particular, the number of those in close proximity affects the photophysical behavior of the resulting polynuclear systems. Therefore, the controlled formation of small clusters of the above metals having defined nuclearities and the study of their structure–property correlations are of great importance in designing functional inorganic materials.

In this regard, polynuclear copper(I) carboxylates exhibiting rich luminescent properties and a remarkable structural diversity have recently attracted our attention. Only a handful of copper(I) carboxylate complexes have been crystallographically characterized to date, all showing unique polynuclear structural arrangements in the solid state. Copper(I) acetate[4] and 2,6-bis(trifluoromethyl)benzoate[5] exhibit 1D polymeric structures based on dicopper units that are further linked by intermolecular copper–oxygen interactions. Copper(I) pivalate has recently been found to exhibit an infinite double-helical chain structure held together by cuprophilicity.[6] In contrast, copper(I) benzoate[7] and trifluoroacetate[8] are composed of tetrameric molecules, in which four copper(I) centers are bridged by carboxylate groups alternately above and below the Cu_4-plane. However, while the former was reported[7] to have discrete tetracopper clusters in the solid state (Scheme 1a), in the latter the tetranuclear units form a polymeric zigzag ribbon (Scheme 1b). This stems from the great electron-withdrawing properties of trifluoroacetate groups that enhance the electrophilicity of the copper(I) centers and enforce additional intermolecular copper–oxygen interactions between the Cu_4-units. Thus, fluorination of carboxylate ligands holding a specific polynuclear copper(I) core together can be an important structure-controlling factor that allows switching on and off of the intermolecular forces between clusters. This effect can be used to manipulate supramolecular assembly processes in the solid state.

The first report on fluorescence of aliphatic copper(I) carboxylates appeared in the literature in 1981,[9] but there have been no follow-up studies on the origin of photoluminescence or structure–property relationships for this class of compounds. The emission maxima of copper(I) formate, acetate, propionate, butyrate, valerate, hexanoate, and heptanoate were found to vary in the broad range of 535–660 nm at room temperature (λ_{ex} = 305–325 nm), but those were not correlated with the structures of the complexes. The photoluminescence of copper(I) pyridylacrylate, $[Cu(3\text{-PYA})]_\infty$, and the water adduct, $[Cu(2\text{-PYA})(H_2O)]_\infty$, both displaying 2D layered structures, was observed at the same wavelength, 580 nm (λ_{ex} = 250 nm), in the solid state.[10] The emission maximum for the recently synthesized copper(I) 2,6-bis(trifluoromethyl)benzoate[5] was measured at 558 nm (λ_{ex} = 350 nm), close to that for analogous copper(I) acetate that emits at 560 nm at room temperature.[9]

Since the reactivity and properties of copper(I) clusters are governed by their molecular structures, in this work we aim to expand the copper(I) carboxylate family and examine the influence of electrophilic substituents of bridging benzoates on the solid state structure of copper(I) complexes. Specifically, we are interested in revealing the effects of a structural type on photophysical properties of the new copper(I) systems, an issue that has not been addressed yet due to the limited number of crystallographically characterized copper(I) carboxylates.

Herein, to access the corresponding copper(I) complexes, we used a homologous set of carboxylate ligands of varied electrophilicity, namely 3-fluorobenzoate, 2,3,4-trifluorobenzoate, and pentafluorobenzoate. The syntheses of new copper(I) complexes were performed by ligand exchange procedures[11,12] based on refluxing copper(I) trifluoroacetate with excess carboxylic acid in benzene (see ESI for experimental procedures†). While ligand



Scheme 1 Tetranuclear copper(I) benzoate (a) and trifluoroacetate (b).

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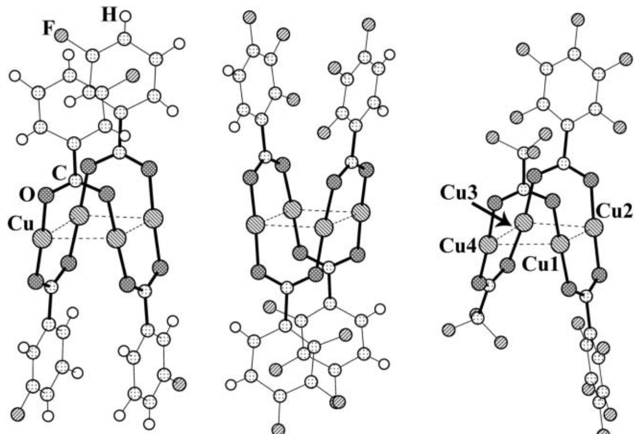
† Electronic supplementary information (ESI) available: Synthesis, characterization, X-ray details, and additional plots of the structures. See DOI: 10.1039/b707957e

substitution was completed in the first two cases to afford [$Cu(O_2C(3\text{-}F)C_6H_4)$] (**1**) and [$Cu(O_2C(2,3,4\text{-}F)_3C_6H_2)$] (**2**), for the latter we initially isolated an intermediate product of the general formula [$Cu(O_2CCF_3)_{1/2}(O_2CC_6F_5)_{1/2}$] (**3**) that has both the parent trifluoroacetate and the new pentafluorobenzoate groups. We have to stress that growing crystals of electrophilic copper(I) complexes from solution is a great challenge due to their avidity for additional coordination[8] and the ease of disproportionation reactions.[13] We overcame these problems by using the micro-scale gas phase deposition technique,[14] which we have already proved to be a very efficient way to avoid interfering solvent effects and to exclude the presence of exogenous ligands during crystallization. Pure crystalline products in the form of colorless blocks have been isolated by sublimation–deposition procedures under reduced pressure in the 220–240 °C range for **1**, 160–220 °C for **2**, and at *ca.* 150 °C for **3**. Complexes **1–3** were fully characterized in the solid state using single crystal X-ray diffraction‡ and spectroscopic techniques (see ESI for more details†).

The structural characterizations of **1–3** revealed that all complexes contain the planar Cu_4-core with carboxylate bridges positioned above and below the plane (Fig. 1). In compound **3**, which incorporates two different carboxylate ligands, pentafluorobenzoate groups bridge the neighboring Cu(1)–Cu(2) and Cu(2)–Cu(3) pairs and trifluoroacetate groups link the neighboring Cu(3)–Cu(4) and Cu(4)–Cu(1) pairs. Importantly, the solid state structures of **1** and **2** are based on the discrete tetracopper units, similar to that of copper(I) benzoate, [$Cu_4(O_2CC_6H_5)_4$] (**4**). At the same time, the mixed carboxylate compound containing very electrophilic trifluoroacetate ligands and fully fluorinated benzoate groups, [$Cu_4(O_2CCF_3)_2(O_2CC_6F_5)_2$] (**3**), is found to be structurally similar to copper(I) trifluoroacetate, [$Cu_4(O_2CCF_3)_4$] (**5**). In contrast to **1** and **2**, complex **3** exhibits a polymeric structure built on intermolecular copper–oxygen interactions in the solid state (Fig. 2).

A close comparison of the newly prepared complexes **1–3** with the previously reported copper(I) benzoate[7] (**4**) and trifluoroacetate[8] (**5**) reveals several noteworthy structural features (ESI†). In general, the Cu···Cu distances in **1–3** are close to the sum of the van der Waals radii (r_{vdW}(Cu) = 1.40 Å)[15] and fall into the category of metallophilic interactions similar to those in Au(I) compounds.[3] The Cu···Cu distances vary to some extent within the [$Cu_4(O_2CR)_4$] series and are longer for complexes containing trifluoroacetate ligands and having extended structures. Thus, the longest Cu···Cu separation between the carboxylate-bridged copper(I) atoms is observed in **3** and **5** (2.832(1) and 2.833(1) Å, respectively). The former compound also has the longest and the shortest Cu···Cu diagonals between the non-bridged metal centers (averaged to 4.822(1) and 2.787(1) Å for two crystallographically unique tetramers). Consequently, the interior Cu–Cu–Cu angles in **3**, averaged to 59.95(3) and 119.67(4)°, are the smallest and the largest angles in this series. Interestingly, the copper(I) atoms in **2** compose a unique rhombic core with equal Cu···Cu distances (2.6895(6) Å), which are the shortest carboxylate-bridged Cu···Cu contacts in the whole family.



1 **2** **3**

Fig. 1 The molecular structures of [$Cu_4(O_2C(3\text{-}F)C_6H_4)_4$] molecule in **1**, [$Cu_4(O_2C(2,3,4\text{-}F)_3C_6H_2)_4$] in **2** and [$Cu_4(O_2CCF_3)_2(O_2CC_6F_5)_2$] in **3**, with the Cu_4-cores shown by dashed lines.

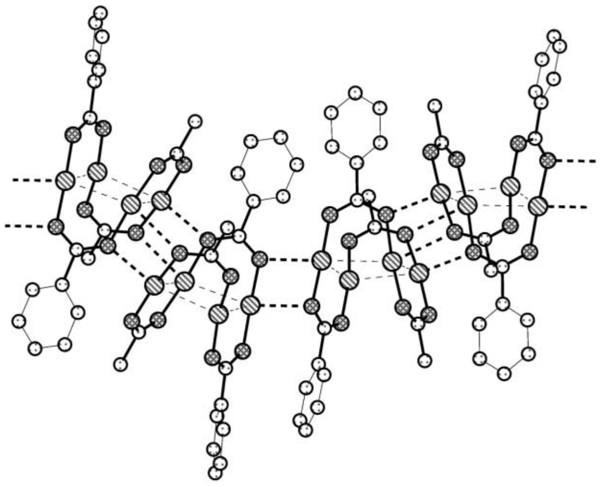


Fig. 2 A fragment of a polymeric chain in [$Cu_4(O_2CCF_3)_2(O_2CC_6F_5)_2$]$_\infty$ (**3**). The F atoms are omitted for clarity.

The average intramolecular Cu–O_{carb} distances are similar in **1** and **2** (1.857(4) and 1.853(2) Å, respectively) and are slightly longer than those in **4** (1.840(15) Å).[7] In **3**, however, the average Cu–O_{carb} bond length of 1.873(4) Å is longer than that in **1** or **2**, but similar to that in **5** (averaged to 1.870(5) Å).[8] The intermolecular copper–oxygen contacts in **3** in the range of 2.405(4)–2.745(4) Å are comparable to those of 2.621(6) Å in **5**.

Complexes **1–3** expand the family of Cu_4-based carboxylates, which now allows for the first analysis of their structure–property relationships. All copper(I) carboxylates **1–3** exhibit yellow-to-green photoluminescence (PL) upon exposure to UV radiation in the solid state. The PL measurements (λ_{ex} = 350 nm) carried out at room temperature on crystalline samples in the range of 250–750 nm revealed broad emission bands centered at 502 nm for **1** and 507 nm for **2**, while λ_{max} for **3** is red-shifted to 583 nm. Thus, the emission wavelengths are very close for the structurally similar complexes [$Cu_4(O_2C(3\text{-}F)C_6H_4)_4$] (**1**) and [$Cu_4(O_2C(2,3,4\text{-}F)_3C_6H_2)_4$] (**2**), having discrete tetranuclear structures. In contrast, the tetramers [$Cu_4(O_2CCF_3)_2(O_2CC_6F_5)_2$]$_\infty$ (**3**) and [$Cu_4(O_2CCF_3)_4$]$_\infty$ (**5**), having analogous polymeric structures in the solid state, both display yellow emission centered at the same wavelength (Fig. 3).

In this work, we have also prepared the fully substituted copper(I) pentafluorobenzoate complex in the single crystalline

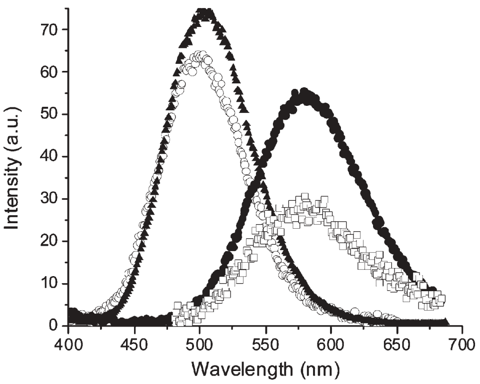


Fig. 3 Photoluminescence spectra of solid samples of **1** (○), **2** (▲), **3** (□), and **5** (●).

form. However, the crystals grew as extremely thin needles and our numerous attempts to find one suitable for an X-ray diffraction analysis were unsuccessful. Interestingly, the crystalline sample of copper(I) pentafluorobenzoate shows emission centered at *ca.* 590 nm (λ_{ex} = 350 nm), close to that of **3** and **5**. We may now speculate that this fact suggests that copper(I) pentafluorobenzoate also has the Cu_4-based extended structure built on Cu···O intermolecular interactions, similar to those of **3** and **5**.

Thus, the current study resulted in the preparation and structural analysis of three new tetranuclear $[Cu_4(O_2CR)_4]$ complexes, of which compounds **1** (R = (3-F)C_6H_4) and **2** (R = (2,3,4-F)$_3C_6H_2$) have discrete molecular structures, while **3** (R = CF_3/C_6F_5) is a polymer based on axial Cu···O interactions analogous to copper(I) trifluoroacetate. The latter two extended structures are good illustrations of the enhancement of intermolecular interactions between isolated copper clusters when ligands with greater electron-withdrawing abilities are used. Control of such individually weak but collectively strong intermolecular interactions can be critical to rational molecular design in supramolecular chemistry.

Importantly, the consideration of photoluminescence properties along with the structural features for the tetranuclear copper(I) clusters revealed that the emission wavelength exhibits a dependence on the structural type (discrete clusters *vs.* extended motifs) for this series. This is the first such observation for the copper(I) carboxylate family, which became possible only after new members of similar structural types were synthesized and crystallographically characterized. To verify the observed trend, we prepared single crystals of copper(I) benzoate, for which the tetranuclear core structure was reported back in 1977.[7] The PL measurements for $[Cu_4(O_2CC_6H_5)_4]$ revealed an emission red-shifted to *ca.* 600 nm (λ_{ex} = 350 nm). Intrigued by this fact, we re-collected the X-ray diffraction experiment and, when analysing the solid state structure of **4**, found its essential difference with that of **1** and **2**. In **4**, there is a close alignment of two crystallographically independent tetramers (ESI, Fig. 4†) with intermolecular copper–copper contacts at 3.239(2) Å (Cu–Cu–Cu angle is 162.35(7)°). These types of interaction were overlooked in the past and are absent in the solid state structures of **1** and **2**.

Our future studies will be aimed at further expansion of the copper(I) carboxylate family and its comprehensive analysis to shed light on how to control the nuclearities, shapes and solid state structures of copper(I) clusters as well as their photoluminescence behavior by selecting a specific metal–ligand combination.

This work was supported by the National Science Foundation Career Award (NSF-0546954) and the Donors of the American Chemical Society Petroleum Research Fund (ACS PRF-42910-AC3).

Notes and references

‡ Crystal data for **1**: $C_{28}H_{16}Cu_4F_4O_8$, *M* = 810.57, monoclinic, *C*2/*c*, *a* = 17.1591(18), *b* = 16.0078(16), *c* = 12.3894(13) Å, β = 129.578(1)°, *V* = 2623.0(5) Å^3, *Z* = 4, *T* = 173(2) K, μ(Mo-Kα) = 3.281 mm^{-1}, 9452 reflections measured, 2302 unique, full-matrix least-squares refinement on F^2 converged at *R*1 = 0.0538 and w*R*2 = 0.1162 for 199 parameters and 1535 reflections with $I > 2\sigma(I)$ (*R*1 = 0.0933, w*R*2 = 0.1321 for all data) and a GOF of 1.061. For **2**: $C_{28}H_8Cu_4F_{12}O_8$, *M* = 954.50, orthorhombic, *Fddd*, *a* = 15.7443(19), *b* = 16.574(2), *c* = 21.682(3) Å, *V* = 5658.1(12) Å^3, *Z* = 8, *T* = 173(2) K, μ(Mo-Kα) = 3.100 mm^{-1}, 11 397 reflections measured, 1706 unique, full-matrix least-squares refinement on F^2 converged at *R*1 = 0.0390 and w*R*2 = 0.0967 for 127 parameters and 1313 reflections with $I > 2\sigma(I)$ (*R*1 = 0.0542, w*R*2 = 0.1074 for all data) and a GOF of 1.015. For **3**: $C_{18}Cu_4F_{16}O_8$, *M* = 902.34, triclinic, $P\bar{1}$, *a* = 11.4301(8), *b* = 14.4443(11), *c* = 16.7589(12) Å, α = 71.969(1), β = 74.374(1), γ = 70.565(1)°, *V* = 2438.0(3) Å^3, *Z* = 4, *T* = 173(2) K, μ(Mo-Kα) = 3.611 mm^{-1}, 21 451 reflections measured, 10 984 unique, full-matrix least-squares refinement on F^2 converged at *R*1 = 0.0538 and w*R*2 = 0.1062 for 865 parameters, 72 restraints, and 6917 reflections with $I > 2\sigma(I)$ (*R*1 = 0.0992, w*R*2 = 0.1241 for all data) and a GOF of 0.961 CCDC 648824–648826. For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b707957e

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