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Insulated copper(I) "wires": structural variations and photoluminescence†

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An unprecedented "molecular wire" type of structure for the copper(I) carboxylate family has been synthesized by utilizing copper–copper interactions and controllable switch of copper–oxygen interactions. Several modifications of the same complex, copper(I) 2,4,6-triisopropylbenzoate, have been isolated to allow evaluation of the structural variation effects on photoluminescent behavior.

Studies of extended metallic chains have been expanding over the past decades due to their potential use as molecular wires.[1] These investigations also offer new insights into development of modern metal–metal bonding theories, understanding of cooperative reactivity of multiple metal centers, and design of metal-rich nanomaterials.[2] Specifically, interactions between the closed d^{10} shells in such networks have attracted very broad attention.[3] Target preparation of linear tri-[4] and tetracopper[5] chains has been reported, along with two extended helical copper(I) polymers held together by cuprophilic Cu···Cu interactions.[6,7] The formation of a copper(I) pivalate helix was explained by a delicate balance between the cuprophilicity and the steric effect of bulky *t*-Bu groups.[6] The helical structure revealed later for copper(I) 3,5-bis-(trifluoromethyl)benzoate[7] can also fit into the above description. However, in contrast to copper(I) pivalate that was found to be nonluminescent, copper(I) 3,5-bis(trifluoromethyl)benzoate exhibits bright luminescence in the solid state.[7] This experimental observation has disproved the explanation provided earlier[6] that the infinite helical arrangement of copper(I) atoms held by cuprophilicity is responsible for the nonradiative decay. Overall, the above two helical polymers stand out in the copper(I) carboxylate family, since all other extended 1D structures are based on intermolecular copper–oxygen interactions.[8–10] These facts prompted us to investigate how the controlled on/off switch of axial copper–oxygen interactions can affect the structural outcome and the resulting photoluminescent behavior.

Among carboxylates, the 2,4,6-triisopropylbenzoate ligand is known to be sufficiently bulky to prevent self-association of dinuclear paddlewheel units.[11] Thus, it was selected in this work to bridge the copper(I) centers and also to favor Cu···Cu instead of Cu···O interactions.

The new copper(I) complex with 2,4,6-triisopropylbenzoate bridges has been synthesized by refluxing copper(I) acetate with an excess of the carboxylic acid in *m*-xylene. The elemental analysis of the product confirmed a $[Cu]:(O_2C_{16}H_{23}) = 1:1$ stoichiometry, suggesting a composition of $[Cu(O_2C_{16}H_{23})]$ (**1**).‡ Sublimation of **1** at 186 °C under reduced pressure yielded very thin colorless needles. Their X-ray diffraction study revealed an essentially linear "copper wire" structure comprised of copper(I) ions bridged by carboxylate groups and further supported by cuprophilic interactions, $[Cu(O_2C_{16}H_{23})]_{\infty,\mathrm{linear}}$ (**2**) (Fig. 1). The Cu···Cu distances of 2.9397(5) Å are comparable to those in helical copper(I) structures (ESI†).[6,7] The Cu–Cu–Cu angles are 159.43(5)°.

An increase of sublimation temperature to 215 °C resulted in the formation of large colorless blocks. Their structural investigation revealed the formation of an extended zigzag "copper wire" $[Cu(O_2C_{16}H_{23})]_{\infty,\mathrm{zigzag}}$ (**3**), having a different spatial distribution of the same structural units as in **2** (Fig. 2).

Although the two polymorphic forms crystallize in different space groups, monoclinic $P2_1/c$ (**2**) *vs.* orthorhombic *Pbcn* (**3**), their cell volumes, normalized by the number of formula units, are essentially the same (382 and 380 $Å^3$ per $[Cu(O_2C_{16}H_{23})]$ in **2** and **3**, respectively). A noticeable shortening of *ca.* 0.06 Å is found for Cu···Cu distances along the chains of **3** in comparison with those of **2**. The Cu···Cu distances in **2** and **3** are significantly shorter than the sum of their van der Waals radii ($r_{\mathrm{vdW}}(\mathrm{Cu})$ = 1.92 Å)[12] and fall into the category of metallophilic interactions, similar to those in Au(I) compounds.[3] The average Cu–O_{carb} distances in **2** and **3** are very similar (1.8445(3) and 1.8483(12) Å, respectively). The zigzag chain **3** is characterized by two Cu–Cu–Cu angles

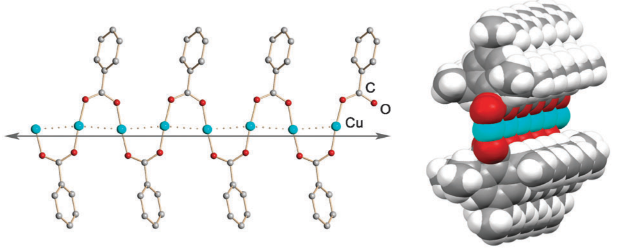

Fig. 1 A fragment of the molecular structure of $[Cu(O_2C_{16}H_{23})]_{\infty,\mathrm{linear}}$ (**2**). Isopropyl groups and hydrogen atoms are omitted for clarity.

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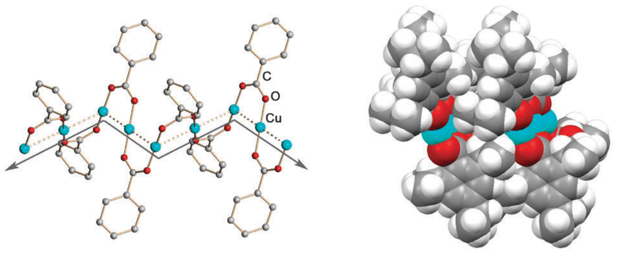

Fig. 2 A fragment of the molecular structure of $[Cu(O_2C_{16}H_{23})]_{\infty,zigzag}$ (**3**). Isopropyl groups and hydrogen atoms are omitted for clarity.

of 96.22(1)° and 180.00(1)°. The dihedral angles between the carboxylic groups and phenyl ring planes are *ca.* 74° and 64° in **2** and **3** in comparison with 69° in the structure of 2,4,6-triisopropylbenzoic acid (ESI†, Fig. S4), showing just a minor steric repulsion effect of neighboring isopropyl groups upon formation of "copper wires".

The individual structural polymorphs of copper(I) 2,4,6-triisopropylbenzoate, **2** and **3**, are reproducibly obtained under controlled experimental conditions. The X-ray powder diffraction (XRPD) data confirmed the structural identity and purity of both bulk crystalline materials (see ESI† for more details). Interestingly, when crystals of **2** or **3** are dissolved in aromatic solvents, such as benzene, toluene or xylenes, they quantitatively transform back to **1**, which under gas phase sublimation conditions re-converts to **2** or **3** (all steps confirmed by XRPD). These conversion procedures can be repeated multiple times along a transformation cycle for the *linear wire* ↔ *zigzag wire* system, depending on the crystallization conditions (Fig. 3).

The X-ray powder diffraction data also demonstrated the structural difference of starting bulk copper(I) 2,4,6-triisopropylbenzoate **1** from **2** and **3** (ESI†, Fig. S7). Importantly, careful consideration of the carboxylate stretches in the IR spectra of all products showed that **2** and **3** are nearly identical but distinctly differ from **1** (ESI†, Fig. S9). Numerous attempts to isolate single crystals by solution crystallization of **1** have resulted in the formation of very thin colorless tangled fibers that were not suitable for the single crystal X-ray diffraction study. Thus, we cannot provide a direct crystallographic proof and can only speculate that copper(I) 2,4,6-triisopropylbenzoate (**1**) exhibits a structure similar to that of copper(I) acetate.[10] The latter consists of dicopper units that are further linked by intermolecular copper–oxygen interactions to form 1D polymeric chains. This conclusion is supported by various experimental data and merits further discussion.

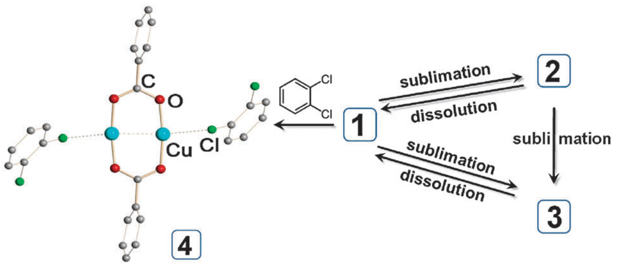

Fig. 3 Schematic representation of synthetic transformations between the forms of $[Cu(O_2C_{16}H_{23})]$. The molecular structure of $[Cu_2(O_2C_{16}H_{23})_2{\cdot}2C_6H_4Cl_2]$ (**4**) is also depicted.

Product **1** is a well-defined chemical compound and cannot be represented as, for example, a random mixture of species, such as oligomeric parts of copper(I) wires, because significant variations in crystallization conditions do not result in any changes of its XRPD and IR fingerprints. Thus, layering solutions of **1** in aromatic solvents (benzene, toluene, or *m*-xylene) with hexanes at room temperature, using low temperature-induced crystallization or heating of the *m*-xylene solution in a sealed ampoule at 215 °C all led to the recovery of unchanged **1** (no solvents are co-crystallized within the crystals). The crystallization attempts are limited to the utilization of aromatic solvents, because dissolution of **1** in strong O- or N-donating solvents results in the immediate disproportionation of the starting material to elemental copper and Cu(II) carboxylate.

Ultimately, although being unable to produce single crystals of **1** from solution, we have crystallized the discrete dimeric product $[Cu_2(O_2C_{16}H_{23})_2{\cdot}2C_6H_4Cl_2]$ (**4**) from *o*-dichlorobenzene at 12 °C. Complex **4** has a Cl-atom of the solvent axially coordinated at both ends of a dicopper(I) unit with the Cu···Cl contacts of 2.895(1) Å (Fig. 3). Moreover, we were able to obtain the single crystal diffraction data for the 2,4,6-triisopropylbenzoate complex of Ag(I), which exhibited a Cu(I) acetate-like structure[10] based on metal–oxygen intermolecular interactions (ESI†, Fig. S12). Importantly, the carboxylate stretches in the IR spectra of **1** and $[Ag_2(O_2C_{16}H_{23})_2]_\infty$ are almost identical, providing strong experimental evidence in favor of the above structural assignment for **1**. In addition, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) data show a close similarity in behavior of **2** and **3** and their noticeable difference from **1**, which is consistent with their overall different solid state structures based on Cu···Cu (**2** and **3**) *vs.* Cu···O interactions (**1**).

The variety of structural forms displayed by copper(I) 2,4,6-triisopropylbenzoate allowed the first analysis of their structure–photoluminescence correlations. Both polymorphs, **2** and **3**, exhibit green-to-orange photoluminescence (PL) upon exposure to UV radiation in the solid state (Fig. 4).

Specifically, the PL measurements (λ_{ex} = 350 nm) carried out at room temperature on crystalline samples revealed an emission λ_{max} at 563 nm (green region) for **2** and a broad peak centered at 610 nm (orange region) for **3**. Interestingly, the

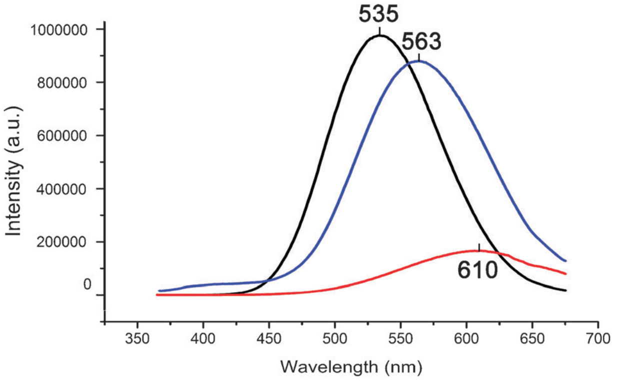

Fig. 4 Solid state PL spectra of **1** (black), **2** (blue), and **3** (red). The emission of **4** is quenched.

emission intensity is substantially greater in the case of the linear "copper wire" compared to the zigzag polymorphic form. Such a drastic difference in PL properties of **2** and **3** (including both the emission wavelength and intensity) shows that relatively small variations in positions of Cu atoms held together by the same bridging ligand may lead to significant changes in photoluminescence. A substantial difference in PL emission of two different polynuclear Cu_4- and Cu_6-core complexes bridged by the same carboxylate has been reported by us recently.[13] However, this is the first instance when two structurally close polymorphs, that differ only by a slightly different arrangement of the same molecular fragments forming a 1D polymeric chain, show very different PL properties.

In contrast to the extended wire-type structures of **2** and **3**, compounds **1** and **4** are based on dinuclear $Cu_2(O_2C_{16}H_{23})_2$ units. The solid sample of **1** brightly emits light with a maximum wavelength of 535 nm, while crystals of **4** show no measurable emission. The latter may be due to the heavy atom effect of the coordinated Cl atoms.[14] Noteworthily, **1** emits light in the same region as the only known benzoate[9] having the same Cu(I) acetate structural type.

This study has revealed structural variations that can be found for carboxylate complexes having the same bridging ligand and the same empirical formula. Changes of experimental conditions allowed us to use isopropyl groups of 2,4,6-triisopropylbenzoate as a controllable switch for intermolecular copper–oxygen interactions and to isolate the previously unknown copper(I) carboxylate wires. The use of gas-phase crystallization for this system proved to be experimentally convenient to turn Cu···O intermolecular interactions off, while solution crystallization put them back on. The consideration of photoluminescent properties for the structurally diverse copper(I) 2,4,6-triisopropylbenzoate products revealed that emission wavelengths and intensities depend not only on the overall structural type (for example, infinite wires *vs.* dimeric structures) but show great sensitivity to subtle differences in spatial distribution of Cu(I) atoms, even for the otherwise similar polymeric chains constructed from the same molecular units (linear *vs.* zigzag wires).

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Notes and references

‡ Synthesis of **1**: a mixture of 0.10 g of copper(I) acetate (0.41 mmol), 0.50 g of 2,4,6-triisopropylbenzoic acid (2.02 mmol) (1 : 2.5) and 0.05 g of metallic copper in 40 mL of *m*-xylene was refluxed for 43 h with a Dean-Stark trap. The obtained light brown solution was filtered through Celite and then concentrated to dryness affording a brown solid. This solid was washed 4 times with hexanes (4 × 10 mL) until it was completely off-white and dried under vacuum at 65 °C for 12 h to provide 0.25 g (99%) of **1**. Anal. Calc. for $C_{16}H_{23}CuO_2$: C, 61.81; H, 7.46. Found: C, 61.72; H, 7.35%. PL (λ_{ex} = 350 nm, λ_{max} = 535 nm).

Crystal data for **2**: $C_{16}H_{23}CuO_2$, M = 310.88, monoclinic, $P2_1/c$, a = 17.979(3), b = 5.7850(10), c = 15.146(3) Å, β = 104.285(3)°, V = 1526.5(5) Å^3, Z = 4, T = 100(2) K, μ(Mo-K$_\alpha$) = 1.426 mm^{-1}, 10 313 reflection measured, 2688 unique, R_{int} = 0.0381, full-matrix least-squares refinement on F^2 converged at R_1 = 0.0609 and wR_2 = 0.1664 for 218 parameters and 2214 reflections with $I > 2\sigma(I)$ (R_1 = 0.0725, wR_2 = 0.1753 for all data) and a GOF of 1.062.

For **3**: $C_{16}H_{23}CuO_2$, M = 310.88, orthorhombic, $Pbcn$, a = 34.687(3), b = 10.2092(8), c = 8.5888(7) Å, V = 3041.5(4)Å^3, Z = 8, T = 100(2) K, μ(Mo-K$_\alpha$) = 1.432 mm^{-1}, 24 294 reflection measured, 3638 unique, R_{int} = 0.0396, full-matrix least-squares refinement on F^2 converged at R_1 = 0.0375 and wR_2 = 0.0966 for 180 parameters and 3228 reflections with $I > 2\sigma(I)$ (R_1 = 0.0425, wR_2 = 0.1003 for all data) and a GOF of 1.086.

For **4**: $C_{44}H_{54}Cl_4Cu_2O_4$, M = 915.77, monoclinic, $P2_1/c$, a = 8.4789(9), b = 11.4630(13), c = 22.026(2) Å, β = 92.125(2), V = 2139.3(4) Å^3, Z = 2, T = 100(2) K, μ(Mo-K$_\alpha$) = 1.285 mm^{-1}, 18 036 reflection measured, 4987 unique, R_{int} = 0.0371, full-matrix least-squares refinement on F^2 converged at R_1 = 0.0341 and wR_2 = 0.0879 for 250 parameters and 4341 reflections with $I > 2\sigma(I)$ (R_1 = 0.0402, wR_2 = 0.0919 for all data) and a GOF of 1.047.

1 J. F. Berry, in *Multiple Bonds Between Metal Atoms*, ed. F. A. Cotton, C. A. Murillo and R. A. Walton, Springer, 2005, pp. 669–706, and references therein; T.-W. Tsai, Q.-R. Huang, S.-M. Peng and B.-Y. Jin, *J. Phys. Chem. C*, 2010, **114**, 3641; V. P. Georgiev and J. E. McGrady, *Inorg. Chem.*, 2010, **49**, 5591.

2 F. A. Cotton, *Chem. Soc. Rev.*, 1983, **12**, 35; M. H. Chisholm and A. M. Macintosh, *Chem. Rev.*, 2005, **105**, 2949; D. L. Phillips, C.-M. Che, K. H. Leung, Z. Mao and M.-C. Tse, *Coord. Chem. Rev.*, 2005, **249**, 1476; A. Grodzicki, I. Lakomska, P. Piszczek, I. Szymanska and E. Szlyk, *Coord. Chem. Rev.*, 2005, **249**, 2232; S. Liu, Y.-F. Han and G.-X. Jin, *Chem. Soc. Rev.*, 2007, **36**, 1543; G. Schmid, *Chem. Soc. Rev.*, 2008, **37**, 1909; A. S. Filatov and M. A. Petrukhina, *Coord. Chem. Rev.*, 2010, **254**, 2234.

3 P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597; P. Pyykkö, *Angew. Chem., Int. Ed.*, 2004, **43**, 4412; A. L. Balch, *Gold Bull.*, 2004, **37**, 45; D. B. Leznoff and J. Lefebvre, *Gold Bull.*, 2005, **38**, 47; S. Sculfort, P. Croizat, A. Messaoudi, M. Benard, M.-M. Rohmer, R. Welter and P. Braunstein, *Angew. Chem., Int. Ed.*, 2009, **48**, 9663.

4 J. Beck and J. Strähle, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 409; G. J. Pyrka, M. El-Mekki and A. A. Pinkerton, *J. Chem. Soc., Chem. Commun.*, 1991, 84.

5 R. Clérac, F. A. Cotton, L. M. Daniels, J. Gu, C. A. Murillo and H.-C. Zhou, *Inorg. Chem.*, 2000, **39**, 4488; Z.-K. Chan, Y.-Y. Wu, J.-D. Chen, C.-Y. Yeh, C.-C. Wang, Y.-F. Tsai and J.-C. Wang, *Dalton Trans.*, 2005, 985; Y. Takemura, T. Nakajima and T. Tanase, *Dalton Trans.*, 2009, 10231.

6 T. Sugiura, H. Yoshikawa and K. Awaga, *Inorg. Chem.*, 2006, **45**, 7584.

7 Y. Sevryugina and M. A. Petrukhina, *Eur. J. Inorg. Chem.*, 2008, 219.

8 F. A. Cotton, E. V. Dikarev and M. A Petrukhina, *Inorg. Chem.*, 2000, **39**, 6072; Y. Sevryugina, O. Hietsoi and M. A. Petrukhina, *Chem. Commun.*, 2007, 3853.

9 Y. Sevryugina, D. D. Vaughn and M. A. Petrukhina, *Inorg. Chim. Acta*, 2007, **360**, 3103.

10 M. G. B. Drew, D. A. Edwards and R. Richards, *J. Chem. Soc., Chem. Commun.*, 1973, 124.

11 R. Clérac, F. A. Cotton, K. R. Dunbar, E. A. Hillard, M. A. Petrukhina and W. B. Smucker, *C. R. Acad. Sci., Ser. IIc: Chim.*, 2001, **4**, 315; F. A. Cotton, E. A. Hillard and C. A. Murillo, *J. Am. Chem. Soc.*, 2002, **124**, 5658.

12 S. S. Batsanov, *Inorg. Mater.*, 2001, **37**, 871; S. Nag, K. Banerjee and D. Datta, *New J. Chem.*, 2007, **31**, 832.

13 A. S. Filatov, O. Hietsoi, Y. Sevryugina, N. N. Gerasimchuk and M. A. Petrukhina, *Inorg. Chem.*, 2010, **49**, 1626.

14 E. F. Healy, S. Manzer, J. Gorman, A. Jones and N. Cristea, *Chem. Phys. Lett.*, 2010, **485**, 258.