Cuprophilic and π-stacking interactions in the formation of supramolecular stacks from dicoordinate organocopper complexes†

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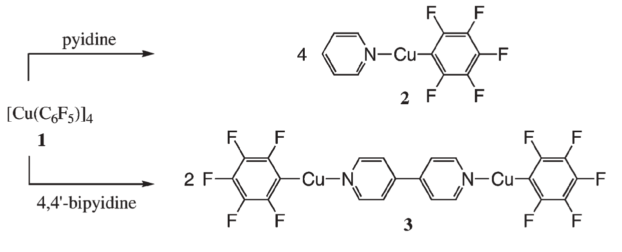
The unsupported organocopper pyridine complexes $C_6F_5Cu(py)$ (2) and $[C_6F_5Cu]_2(4,4'\text{-bipy})$ (3) form supramolecular structures that are unprecedented in organocopper chemistry; one-dimensional chains of copper atoms with Cu···Cu distances of 2.8924(3) Å in the blue-luminescent complex 2 are likely associated with cuprophilic interactions, whereas multiple perfluoroarene–arene interactions dominate in the supramolecular assembly of 3.

Organocopper compounds form an intriguing variety of interesting aggregates in the solid state as well as in solution.[1] To date, a number of well-defined homoleptic arylcopper species $[ArCu]_n$ with varying degrees of association ($n = 2$–$8, \infty$) have been isolated and structurally characterized.[1] Aggregation typically occurs through bridging of two copper centers with an organic moiety.[1] It is also well-known that treatment of organocopper species with strongly coordinating ligands (L) can lead to break-down of the aggregated structure.[2] We show here a new case where, even though aggregate break-down leads to formally dicoordinate organocopper complexes RCuL, cuprophilic and π-stacking interactions result in formation of supramolecular structures in the solid state.

Pentafluorophenylcopper tetramer ($[C_6F_5Cu]_4$; **1**)[3–5] was treated with an equimolar amount of pyridine at ambient temperature. Pale yellow crystals of **2** were obtained from CH_2Cl_2 solution at −38 °C in 81% isolated yield. Slow diffusion of a solution of 4,4′-bipyridine in CH_2Cl_2 into a solution of **1** in CH_2Cl_2 led to precipitation of **3** as a light-yellow solid (yield: 87%), which is only sparingly soluble in non-coordinating solvents.



The coordination of pyridine and 4,4′-bipyridine to copper was confirmed by multinuclear NMR spectroscopy and the composition of **3** as a 2 : 1 complex of C_6F_5Cu and 4,4′-bipyridine was verified by elemental analysis. The strong decrease in the chemical shift difference $\Delta\delta(^{19}F_{meta/para})$ from 16.6 ppm in **1** to 3.1 ppm for **2** and 2.7 ppm for **3** in the ^{19}F NMR spectra is characteristic of coordination of nucleophiles and break-down of the tetrameric aggregate.[4] Low temperature NMR spectroscopy of **2** showed no evidence of a dynamic process down to −80 °C.

Complex **2** is thermally stable to *ca.* 150 °C and the polymorphs of **3** start to decompose above 130 °C. Coordination of the pyridine ligand thus leads to destabilization of the pentafluorophenylcopper complex in comparison to the dioxane complex of **1** with T_{dec} = 200–220 °C.[3] Indeed, the isolation and crystallographic characterization of organocopper pyridine complexes have been hampered in the past by their relatively low thermal stability.[2a]

Crystal structures of complex **2** and of two polymorphs of **3** were obtained (Fig. 1–3).†‡ The structure of **2** is unusual in that all atoms, including the hydrogen atoms, reside on a crystallographic mirror plane. The copper centers adopt in all three structures a linear or nearly linear coordination geometry (**2**: 178.54(6)°; **3-α**: 180°; **3-β**: 178.17(8)°) and thus represent rare examples of structurally characterized dicoordinate organocopper complexes RCuL. The pentafluorophenyl groups and the pyridine rings are either perfectly coplanar or nearly so (**2**: 0.0°; **3-α**: 3.8°; **3-β**: 9.5°). The two structures of **3** differ mainly in the twist at the central C–C bond connecting the two pyridine rings; for **3-α** an interplanar angle of 44.3° is observed, whereas the pyridine rings in **3-β** adopt a coplanar conformation. The copper–carbon bonds of 1.8913(17) Å for **2**, 1.880(4) Å for **3-α** and 1.890(2) Å for **3-β** are shorter than those in the tetrameric precursor **1** (1.957 Å to 2.145 Å)

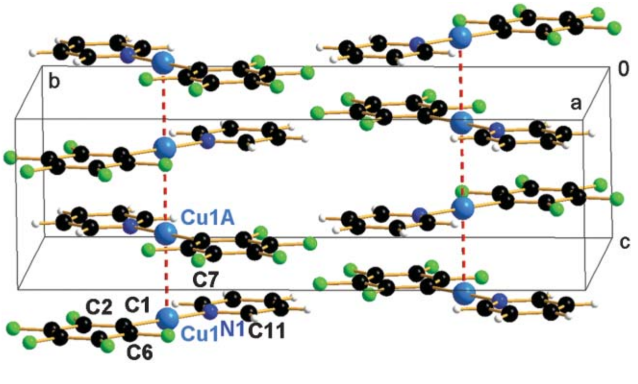


Fig. 1 Packing diagram of **2**. Selected interatomic distances (Å) and angles (°) for **2**: Cu1–C1 1.8913(17), Cu1–N1 1.9022(15), Cu1···Cu1A 2.8924(3), C1–Cu1–N1 178.54(6), C7–N1–Cu1 121.11(12), C11–N1–Cu1 121.30(11), C6–C1–Cu1 121.80(13), C2–C1–Cu1 124.61(14), C1–Cu1···Cu1A 89.900(5), N1–Cu1···Cu1A 90.097(5), Cu1···Cu1A···Cu1B 179.716(15).

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† Electronic supplementary information (ESI) available: experimental details, Ortep plots of **2**, **3-α**, **3-β**, a packing diagram of **2**. See http://www.rsc.org/suppdata/cc/b4/b417532h/

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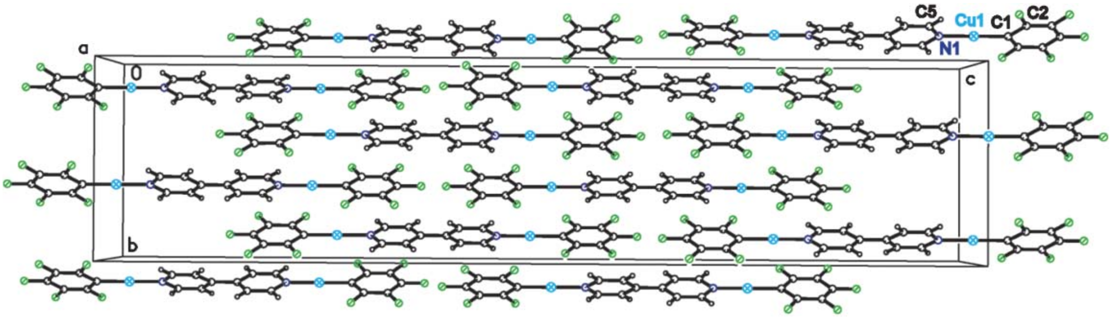

Fig. 2 Packing diagram of **3-α**. Selected interatomic distances (Å) and angles (°) for **3-α**: Cu1–C1 1.880(4), Cu1–N1 1.902(3), N1–C5 1.347(3), C1–Cu1–N1 180.0, C5–N1–Cu1 121.3(2), C2–C1–Cu1 123.3(2).

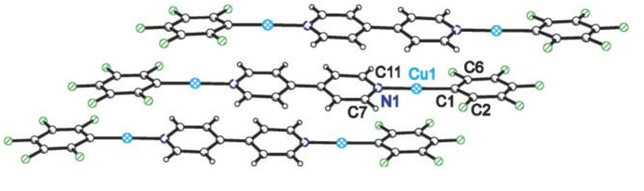

Fig. 3 Overlap diagram of three molecules of **3-β**. Selected interatomic distances (Å) and angles (°) for **3-β**: Cu1–C1 1.890(2), Cu1–N1 1.903(2), N1–C7 1.324(3), N1–C11 1.327(3), C1–Cu1–N1 178.17(8), C7–N1–Cu1 121.0(2), C11–N1–Cu1 122.4(2), C2–C1–Cu1 124.1(2), C6–C1–Cu1 122.4(2).

and Power's monomeric arylcopper solvate [C_6H_2-2,4,6-*t*-$Bu_3Cu(Me_2S)$].[6] However, they are similar to those found by van Koten *et al.* for a dimeric complex containing a chelating oxazolinyl group (Cu–C = 1.899(5) Å).[7] The copper–nitrogen distances are in a very narrow range from 1.902–1.903 Å and are comparable to those in the oxazolinyl complex[7] (Cu–N 1.902(4) Å) and a related pyridylalkyl species [2-$(SiMe_3)_2C(Cu)C_5H_4N]_2$[8] (Cu–N = 1.910(3) Å).

Inspection of the extended structures of these dicoordinate copper species shows that aggregation leads to supramolecular stacks that are unprecedented in organocopper chemistry. Intriguingly, the copper atoms in **2** are arranged in one-dimensional chains with Cu···Cu distances of 2.8924(3) Å, which are among the shortest reported for unsupported $Cu^I\cdots Cu^I$ contacts (Fig. 1).[9] Moreover, **2** represents the first structure of an organocopper species that is aggregated into linear metal chains extending throughout the entire crystal lattice.[10] Only two examples of linear polymeric copper chains, $[Cu(NH_3)_2]^+$ Br^- and $[Cu_2terpy_2]^{2+}$ $2X^-$ (terpy = terpyridine),[11,12] have been reported previously. The $Cu^I\cdots Cu^I$ distances in **2** are similar to those reported by Wagner and co-workers for $\{[Cu(NH_3)_2]Br\}_n$ (2.931(1) Å).[11] In contrast to these ionic Cu^I complexes, in which the counterions X^- may play a significant role in the bonding,[9] the individual units in **2** are neutral RCuL fragments.

The ligands in adjacent RCuL units of **2** adopt a staggered conformation thus avoiding any π-stacking interactions.[13,14] In contrast, both crystallographically characterized polymorphs of **3**, **3-α** and **3-β**, show supramolecular two-dimensional stacks as a result of multiple perfluoroarene–arene π-interactions[15] (Fig. 2 and Fig. 3). The observed supramolecular isomerism[16] may be traced back to the flexibility of the central carbon–carbon bond within the bipyridyl spacer and the linear and near-planar geometry of the C_6F_5–Cu–Py fragments. The pentafluorophenyl groups in **3-α** are coplanar to the pyridine rings of adjacent molecules and *vice versa* providing a total of eight arene–perfluoroarene interactions per molecule. The interplanar distance between the aromatic rings amounts to *ca.* 3.5 Å, typical of strong arene–arene π-stacking interactions.[17] While the copper atoms are also aligned in **3-α**, the Cu···Cu distances of 3.639 Å are much longer than those in **2**. A zigzag arrangement of the copper atoms results from a slight lateral slippage of the aryl groups typical of perfluoroarene–arene stacks with an angle of 70.8° between the molecular and the stacking axis (angle Cu···Cu1–C1). The polymorph **3-β** shows very long Cu···Cu distances of 5.033 Å (Fig. 3). The longer Cu···Cu distances in **3-β** compared to **3-α** can be traced back to a much larger offset between the aromatic rings that results in alignment of the copper atoms at an angle of 43.4° relative to the plane of the molecules.

Based on the short Cu···Cu contacts in **2**, which are close to the sum of the van der Waals radii of Cu^I centers of 2.80 Å,[18] the presence of so-called "cuprophilic" interactions has to be considered. Aurophilic and argentophilic interactions, the attractive forces between closed-shell d^{10} metal ions of gold and silver, have long been recognized and are now commonly accepted.[19] Attractive interactions between closed-shell $Cu^I\cdots Cu^I$ pairs on the other hand have only recently been proposed based on experimental and theoretical studies, and the existence of such interactions is still highly controversial.[9] Based on MP2 calculations Schwerdtfeger *et al.* determined that cuprophilic interactions between neutral pairs $[RCuL]_2$ should be attractive by up to -4 kcal mol^{-1}, and that the interaction potential for cuprophilic interactions is very shallow in the range from *ca.* 2.5 to 3.5 Å.[20] Cuprophilic interactions are therefore likely to be present in **2** and may also weakly contribute to the overall intermolecular attractive forces in **3-α**. The latter are, however, certainly to a large extent governed by the multiple perfluoroarene–arene interactions, and perfluoroarene–arene interactions are overruling any attractive forces between the copper centers in **3-β**.

Preliminary photophysical studies show that **2** displays strong blue luminescence (λ_{max} = 460 nm) in the solid state at RT upon excitation at λ = 330 nm (Fig. 4). A weaker long-lived emission band extends to *ca.* 700 nm. In contrast, the polymorphs **3-α** and **3-β** are non-emissive at RT and no luminescence was found for **2** at RT in solution. The photophysical properties of Cu^I aggregates have previously been discussed in context with cuprophilic interactions.[21] For instance, concentration dependent luminescence has recently been reported for a trimeric copper pyrazole complex, $\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$.[22] Moreover, the rich photoluminescent

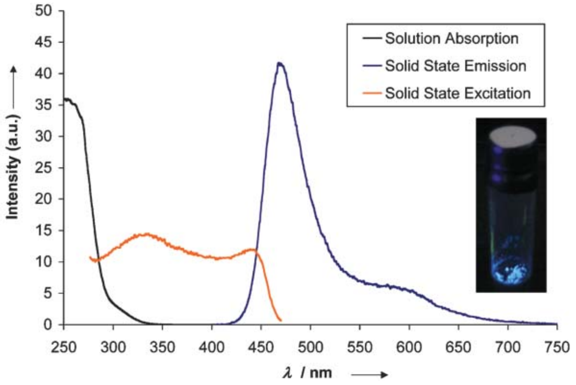

Fig. 4 Solution absorption and solid-state excitation (λ_{em} = 460 nm) and emission spectra (λ_{exc} = 330 nm) of **2** at RT.

behavior of stacks and extended chains of related Ag^I and Au^I species is commonly attributed to the presence of short intermolecular contacts.[23] The solid-state luminescence of $[Au(2\text{-py})]_3$, for example, has been related to the supramolecular aggregation of individual trimers into offset stacks through short intermolecular Au···Au distances of 3.146(3) and 3.105(2) Å based on a comparison of solid state and solution properties.[24] Further studies on the origin of the photoluminescent behavior of **2** including low temperature measurements are currently in progress and will likely provide insight into whether the luminescent properties of **2** may be related to the presence of short copper–copper contacts.

In conclusion, coordination of pyridine or 4,4′-bipyridine results in complete breakdown of the tetrameric structure of **1**, but cuprophilic and multiple perfluoroarene–arene interactions in turn lead to the formation of novel supramolecular structures and, in the case of **2**, the alignment of the copper atoms in one-dimensional chains. Intriguingly, a comparison of the structures of **2** and **3** indicates that significant cuprophilic interactions in these compounds are observed only if π-stacking between the aromatic substituents is avoided as in **2**. In the solid state **2** shows intense blue luminescence, the origin of which we are currently further investigating.

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Notes and references

‡ Crystallographic details are given in the Electronic Supplementary Information (ESI), and CCDC-250638, CCDC-219364, and CCDC-219363 contain the crystallographic data for **2**, **3-α**, and **3-β**, respectively. These data can be obtained online free of charge *via* www.ccdc.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk). See http://www.rsc.org/suppdata/cc/b4/b417532h/ for crystallographic data in .cif or other electronic format.

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