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A novel luminescent copper(I) complex containing an acetylenediide-bridged, butterfly-shaped tetranuclear core

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A novel luminescent acetylenediide-bridged tetranuclear copper(I) complex [Cu_4(μ-Ph_2Ppypz)$_4$(μ$_4$-η^1,η^2-C≡C)](ClO_4)$_2$ [Ph_2Ppypz = 2-(diphenylphosphino-6-pyrazol-1-yl)pyridine] has been synthesized and structurally characterized by X-ray crystallography.

Metal acetylides have been subjected to intensive study for many years.[1] The interest mainly stems from: (i) the ability of the acetylide group to bond to transition metals, forming a growing number of mono- and poly-nuclear complexes that display an unusually rich variety of structures; (ii) the versatile reactivity of the coordinated acetylide group in its complexes, which serve as useful precursors for the synthesis of other target organometallic compounds. In contrast to the plethora of ethynyl complexes containing acetylenide ligands of the type R–C≡C$^-$, ethynediyl complexes containing the acetylenediide ligand, C_2^{2-}, that exhibits the known coordination modes[2] shown in Fig. 1 are relatively rare.

The group 11 metal acetylides M_2C_2 exhibit properties that are characteristic of covalent polymeric solids. They are insoluble in many common solvents, and highly explosive and sensitive to mechanical shock when completely dried. Some examples of (μ-C≡C)bis[(phosphine)gold(I)] complexes have been reported.[3] In these complexes, the C_2^{2-} anion coordinates a pair of gold atoms by σ-bonding to form a linear molecule. Double salts of silver(I) acetylide were studied over half a century ago,[1a] and recently several novel triple and quadruple salts have been synthesized.[5d,e] Their structures exhibit a variety of polyhedral silver cages each encapsulating a C_2^{2-} anion ($C_2@Ag_n$, n = 6, 7, 8, 9).[5] In the context of the chemistry of copper(I) acetylide, development has been hampered by its insolubility in common solvents and the lack of general methods for the synthesis of its derivatives. To date, there is only one known ethynediyl copper(I) complex, namely [Cu_4(μ-dppm)$_4$(μ$_4$-η^1,η^2-C≡C)](BF_4)$_2$ [dppm = bis(diphenylphosphino)methane] **1** where the C_2^{2-} anion coordinates four rectangularly arranged copper atoms by distinct σ and π bonding, and this planar **D**(1) coordination mode is illustrated in Fig. 1.[6a] Here we report the synthesis, structure and luminescence properties of a related complex [Cu_4(μ-Ph_2Ppypz)$_4$(μ$_4$-η^1,η^2-C≡C)](ClO_4)$_2$ [Ph_2Ppypz = 2-(diphenylphosphino-6-pyrazol-1-yl)pyridine] **2**, in which the coordination mode of C_2^{2-} is **D**(2), with the metal atoms arranged about it in a butterfly configuration.

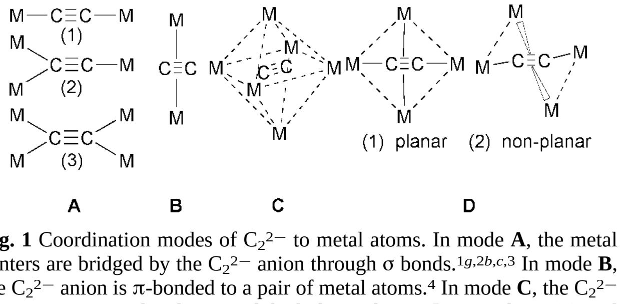
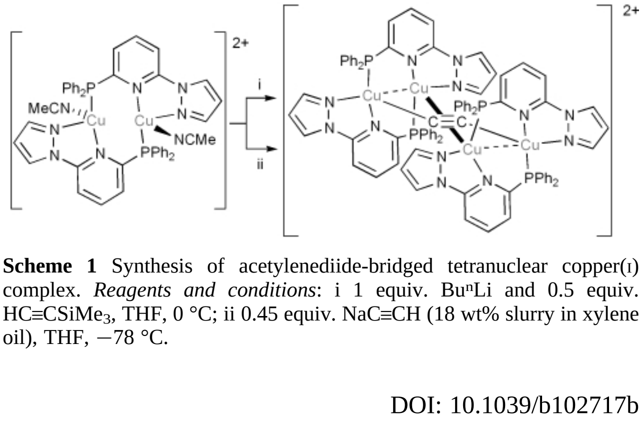


Fig. 1 Coordination modes of C_2^{2-} to metal atoms. In mode **A**, the metal centers are bridged by the C_2^{2-} anion through σ bonds.[1g,2b,c,3] In mode **B**, the C_2^{2-} anion is π-bonded to a pair of metal atoms.[4] In mode **C**, the C_2^{2-} species is encapsulated in a polyhedral metal cage.[5] In modes **D**(1) and **D**(2), the metal atoms are bridged by the C_2^{2-} anion through distinct σ and π bonds in a planar[6] and non-planar[5b] configuration, respectively.

The synthesis of **2** is shown in Scheme 1. In the first method, 1 equiv. Bu^{n}Li was added at room temperature to a solution of 0.5 equiv. Me_3SiC≡CH in pre-dried, degassed THF under an inert nitrogen atmosphere, and 1 equiv. [Cu_2(μ-Ph_2Ppypz)$_2$(MeCN)$_2$](ClO_4)$_2$ was then introduced with stirring. After evaporation to dryness, the resulting solid was extracted with CH_2Cl_2. Subsequent diffusion of diisopropyl ether into the concentrated solution gave air-stable orange crystals of **2**·3CH_2Cl_2. In the second method, 0.45 equiv. NaC≡CH was added to a solution of 1 equiv. [Cu_2(μ-Ph_2Ppypz)$_2$(MeCN)$_2$](ClO_4)$_2$[7a] in degassed THF at −78 °C under an inert atmosphere of nitrogen, and the solution was stirred for 24 h at room temperature. The work-up was similar to that in the first method. However, the yield of the second method is very low (< 10%) due to formation of Cu_2C_2 as the major product. The much higher yield by the first method (60%) is attributable to the gradual release of C_2^{2-} from Me_3SiC≡C$^-$. Complex **2** gave satisfactory C,H,N analyses, and was subsequently characterized by $^{13}C\{^1H\}$ NMR spectroscopy and X-ray crystallography.† In the $^{13}C\{^1H\}$ NMR (CD_2Cl_2) spectrum, the resonance for carbon in the –C≡C– group appeared at δ 68.65, comparable with that in C_2H_2 (δ 71.90). Although the C≡C stretching vibration is IR active in coordination mode **D**(2), the intensity is weak and scarcely observable in the IR spectrum.

Fig. 2 shows a perspective drawing of the tetranuclear cation in **2**·3CH_2Cl_2 with the atomic numbering scheme. The cation has crystallographic C_2 symmetry. Its structure consists of a butterfly-shaped tetranuclear Cu_4C_2 core in which the acetylenediide anion bridges a pair of Cu_2 sub-units in both η^1 and η^2 bonding modes. The normal electron count requires that the C_2^{2-} anion acts as a six-electron donor according to the covalent model. While the interaction of the C_2^{2-} anion with each Cu_2 sub-unit resembles that found in other μ-η^1,η^2-acetylido complexes, best overlap of the two π orbitals of the C_2^{2-} ligand with the metal orbitals would require that the two Cu_2 sub-units be orthogonal to each other. As shown in Fig. 2, the Cu(2)–C(1)–C(1A)–Cu(2A) system is approximately linear, and the dihedral angle between the planes Cu(1)–C(1)–C(1A) and Cu(1A)–C(1)–C(1A) is 129.0(3)°, which is very distinct



Scheme 1 Synthesis of acetylenediide-bridged tetranuclear copper(I) complex. *Reagents and conditions*: i 1 equiv. Bu^{n}Li and 0.5 equiv. HC≡CSiMe$_3$, THF, 0 °C; ii 0.45 equiv. NaC≡CH (18 wt% slurry in xylene oil), THF, −78 °C.

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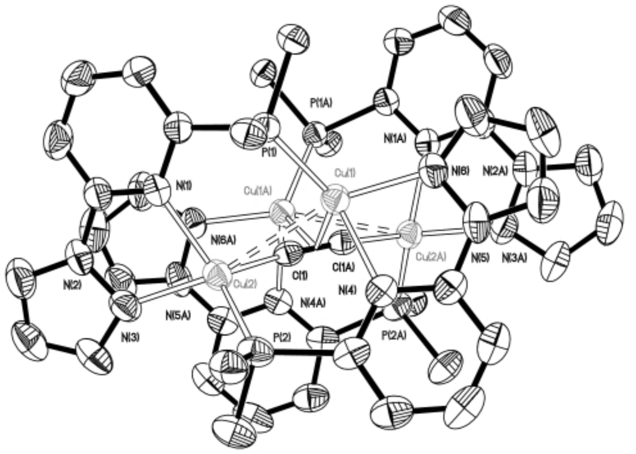

Fig. 2 Perspective drawing (thermal ellipsoids at 35% probability level) of the tetranuclear copper(I) cation in $\mathbf{2}\cdot 3CH_2Cl_2$ with the atomic numbering scheme. Hydrogen atoms and phenyl rings have been omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–C(1) 2.143(6), Cu(1)–C(1A) 2.215(6), Cu(2)–C(1) 1.931(6), Cu(1)–Cu(2) 2.843(1), C(1)–C(1A) 1.26(1), Cu(1)–P(1) 2.220(2), Cu(1)–N(4) 2.244(5), Cu(1)–N(6) 2.050(5), Cu(2)–P(2) 2.217(2), Cu(2)–N(1) 2.116(5), Cu(2)–N(3) 2.104(5), Cu(1)–C(1)–C(1A) 76.3(5), Cu(2)–C(1)–C(1A) 160.9(7), dihedral angle between planes Cu(1)–C(1)–C(1A) and Cu(1A)–C(1A)–C(1) 129.0(3)°. Symmetry code: A $-x, y, \frac{1}{2} - z$.

from the planar Cu_4C_2 core in **1**. A plausible reason is that the pyridinopyrazole group has less steric hindrance than the dppm group. The C≡C bond in **2** [1.26(1) Å] is identical to that in **1** but longer than those (1.15–1.22 Å) in the ethynediyl silver and gold complexes. The shortest copper–copper distance Cu(1)–Cu(2) 2.843(1) Å lies between those in $[Cu_2(\mu\text{-}Ph_2Ppypz)_2(\mu\text{-}C{\equiv}CPh)](ClO_4)$ [2.516(1) Å] and **1** [3.264(2) and 3.245(2) Å], which is suggestive of cuprophilic interaction between the copper(I) centers.[8] The coordination number of each copper atom in **2** is four, in contrast to the coordination number of three in **1**. The reason can also be attributed to the difference in steric bulk of the two ligands. The dppm ligand is soft and bulky, and the binuclear complex $[Cu_2(MeCN)_4(dppm)_2](BF_4)_2$ readily reacts with halide or $RC{\equiv}C^-$ to form a trinuclear complex.[9] On the other hand, Ph_2Ppypz is more rigid and $[Cu_2(MeCN)_2(Ph_2Ppypz)_2](ClO_4)_2$ reacts with halide or $RC{\equiv}C^-$ to form other binuclear products.[7]

The electronic absorption and emission spectra of complex **2** in CH_2Cl_2 are shown in Fig. 3.‡ The electronic spectrum exhibits absorption bands at *ca.* 340–400 nm (λ_{max}^{abs}/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}), 345sh (100 000), 364sh (63 827), 373 (37 675), 396 (28 400)). A similar band is also observed in **1** at 374 nm. Such bands most likely involve the Cu_4C_2 core, so they are assigned to LMCT bands of $[(C{\equiv}C)^{2-}{\rightarrow}Cu_4]$. Excitation of **2** in dichloromethane at $\lambda > 350$ nm produces blue–green luminescence (408, 430, 448sh, 475sh nm). Vibronically structured bands with two progressional spacings at 2188 and 2203 cm^{-1}, characteristic of the ν(C≡C) stretch,[9b–d] were observed. The appearance of vibrational progressions is suggestive of involvement of the C_2^{2-} unit in the excited state. The overlap of the emission bands with the low-energy excitation bands and a quite small Stokes shift, quite distinct from the case in **1**, are assigned to the rigid and unsubstituted aromatic ring of Ph_2Ppypz. A possible origin of the emission involves emissive states derived from $[(C{\equiv}C)^{2-}{\rightarrow}Cu_4]$ LMCT mixed with d→s character. Similar assignments have been proposed for other alkynyl/alkynediyl copper(I)/silver(I) systems.[9]

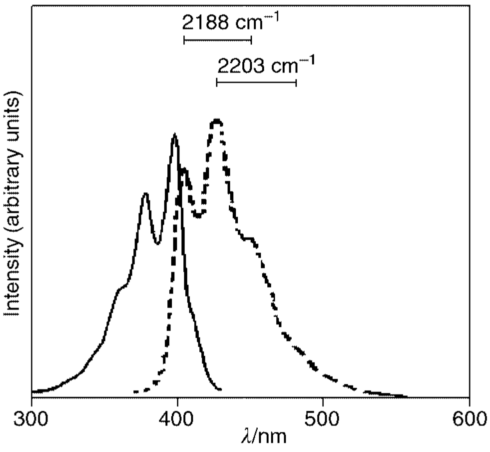

Fig. 3 Excitation spectrum (left, ——) and emission spectrum (right, - - - -) of **2** in CH_2Cl_2 at 298 K.

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Notes and references

† *Crystal data* for compound **2**: $C_{82}H_{64}Cl_2Cu_4N_{12}O_8P_4\cdot 3CH_2Cl_2$, M = 2049.17, monoclinic, space group $C2/c$ (no. 15), a = 21.343(9), b = 17.303(8), c = 26.26(1) Å, β = 97.79(1)°, V = 9607(7) Å^3, Z = 4, D_c = 1.417 Mg m^{-3}, $F(000)$ = 4160, μ(Mo-Kα) = 1.22 mm^{-1}, 25902 reflections measured, 8484 unique (R_{int} = 0.061), final $R1$ = 0.055, $wR2$ = 0.152 for 8484 independent reflections [$I > 2\sigma(I)$]. Data collection was performed at 293 K on a Bruker SMART 1000 CCD diffractometer using frames of oscillation range 0.3°, with $1.5 < \theta < 25°$. CCDC reference number 160440.

See http://www.rsc.org/suppdata/cc/b1/b102717b/ for crystallographic data in CIF or other electronic format.

‡ The emission and excitation spectra were obtained with a RF-540 fluorimeter (conc. 10^{-5} mol dm^{-3}, CH_2Cl_2). The excitation wavelength was 368 nm.

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