A novel luminescent tetranuclear copper(I) acetylide with open-cube structure

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A novel luminescent tetranuclear copper(I) acetylide $[Cu_4(PPh_3)_4(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}CC_6H_4OMe\text{-}p)_3]^+$ 1 with open-cube structure is synthesized and its photoredox activities studied; the X-ray crystal structure of 1 is also reported.

There have been a number of reports on the studies of luminescent polynuclear d^{10} copper(I) clusters,[1] while related studies on the organocopper(I) counterparts are relatively rare[2] even though a wide diversity of organocopper(I) systems with interesting structures exist.[2,3] In view of our efforts on the design, preparation and luminescence studies of acetylide-bridged polynuclear d^{10} metal complexes,[2a–f] a novel tetranuclear copper(I) cluster, $[Cu_4(PPh_3)_4(\mu_3\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}CC_6H_4OMe\text{-}p)_3]^+$ **1** with an open-cube structure has been successfully prepared and crystallographically characterized.

Reaction of $[Cu(MeCN)_4]PF_6$ with triphenylphosphine and $[\{Au(C{\equiv}CC_6H_4OMe\text{-}p)\}_n]$ in dichloromethane under a stream of dry nitrogen afforded **1**, isolated as air-stable pale yellow crystals in *ca.* 70% yield, and $[Au(PPh_3)_2]^+$, as a by-product. Complex **1** is stable in the solid state, while in dichloromethane and acetone solutions, it is stable only for a few weeks in the absence of light. The newly synthesized copper(I) complex gave satisfactory elemental analyses, and has been characterized by ^1H and ^{31}P NMR spectroscopy, positive FAB mass spectrometry,† and X-ray crystallography.‡

Fig. 1 shows a perspective drawing of the cation of **1**. The tetranuclear complex essentially adopts a cubane structure, such as that of $[Cu_4X_4L_4]$ (X = halogen, L = N, P, As donors),[4] with a vertex missing. Such an open-cube M_4 structure, though known in a number of metal clusters such as those of iron and molybdenum, is rarely found in copper(I).[5] To the best of our knowledge, the only known examples are those found in $[Cu_4Cl(PPh_2)_3(PPr^nPh_2)_3]$[6a] and $[Cu_4(PPh_2)_3Cl(PMe_3)_4]$[6b] with no precedent in acetylide complexes. It consists of a puckered Cu_3C_3 six-membered ring, which is bridged by Cu(1) and with the C≡C moiety of the acetylide groups in μ_3-bridging modes. The Cu(1)–Cu(2), Cu(1)–Cu(3) and Cu(1)–Cu(4) distances of 2.446(2)–2.467(2)Å, are found to be much shorter than the Cu···Cu distances found within the Cu_3C_3 puckered ring (3.79–3.85Å), and are suggestive of the electron deficient nature of the two-electron–three-centre Cu(1)–C–Cu bonding. The acute Cu(1)–C–Cu angles of 70.0(4)–73.9(4)° further indicate the electron deficiency of these two-electron–three-centre bonds. On the other hand, the Cu atoms in the Cu_3C_3 ring are relatively less electron deficient owing to the fact that the two-electron–three-centre Cu–C–Cu bonding is complemented by a side-on C≡C binding to each of the Cu centres in the ring. Interestingly, the structure of **1** differs from that of a related organocopper(I) cluster, $[Cu_4\{P(C_6H_5Me\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$,[2c] which has a distorted close-cubane geometry, although the constituents of the complexes are similar. The Cu···Cu distances for **1** are in the range 2.446(2)–2.467(2) Å, comparable to those found in $[Cu_4(PPh_2)_3Cl(PMe_3)_4]$ [2.4836(8)–2.5345(8)Å][6b] but shorter than those found in the close-cubane-type $[Cu(PPh_3)X]_4$ (X = Cl, Br, I) [2.874(5)–3.541(2)Å][4b,d] and $[Cu_4(PAr_3)_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$ (Ar = Ph, $C_6H_4F\text{-}p$, $C_6H_4Me\text{-}p$) [2.5092(5)–2.6635(8)Å].[2c] Such short Cu···Cu distances are not uncommon in organocopper systems and may not necessarily indicate a significant metal–metal interaction.[3,7] The presence of side-on π-bonding between the C≡C groups and the copper(I) centres gave rise to the bent C≡C–C bonds [C(1)–C(2)–C(7) 162(1), C(3)–C(4)–C(14) 163(1), C(5)–C(6)–C(21) 165(1)°].

The room-temperature electronic absorption spectra of **1** in dichloromethane solution is characterized by a high-energy absorption shoulder at *ca.* 252 nm (ε 88 550 $dm^3\ mol^{-1}\ cm^{-1}$) and a peak at *ca.* 330 (48925). Excitation of solid **1** or its fluid solutions at $\lambda > 350$ nm results in long-lived, intense luminescence. A solid sample of **1** emits at 445 nm at both room temperature and 77 K, with a weaker shoulder at *ca.* 630 nm ($\tau_0 = 20.7 \pm 1.0$ μs) in the room-temperature luminescence, while the emission spectra of **1** in degassed acetone and dichloromethane solutions show an intense band at *ca.* 675 nm (acetone, $\tau_0 = 4.0 \pm 0.4$ μs; CH_2Cl_2, $\tau_0 = 2.7 \pm 0.3$ μs). The long emissive lifetime in the microsecond range is suggestive of emissive states of triplet parentage. With reference to our previous spectroscopic work on related polynuclear copper(I) acetylide systems[2a–f] and the presence of short Cu···Cu distances observed in **1**, it is likely that the low-energy emission at 630–675 nm is derived from states involving $C{\equiv}CC_6H_4OMe\text{-}p \longrightarrow Cu_4$ ligand-to-metal charge transfer LMCT character, with mixing of a metal centred d–s state.

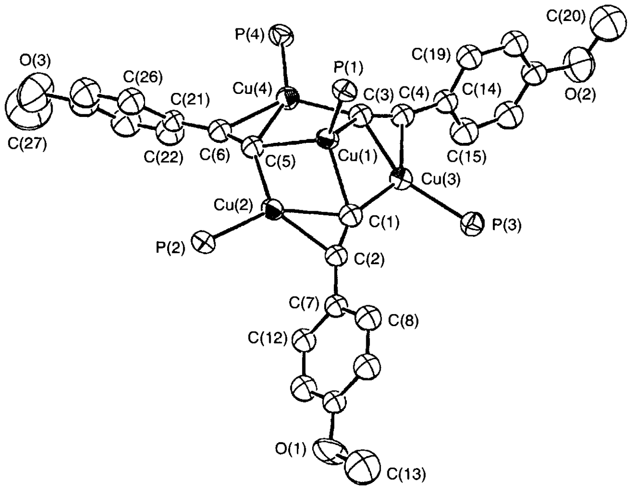

Fig. 1 Perspective view of the cation of **1** with atomic numbering scheme. Thermal ellipsoids are at the 25% probability level. The phenyl rings attached to the phosphorus atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Cu(1)–Cu(2) 2.446(2), Cu(1)–Cu(3) 2.461(2), Cu(1)–Cu(4), 2.467(2), Cu(1)–P(1) 2.253(4), Cu(1)–C(1) 2.13(1), Cu(1)–C(3) 2.10(1), Cu(1)–C(5) 2.13(1), Cu(2)–C(1) 2.13(1), Cu(2)–C(2) 2.11(1), Cu(2)–C(5) 2.03(1), Cu(3)–C(1) 2.03(1), Cu(3)–C(3) 2.11(1), Cu(3)–C(4) 2.13(1), Cu(4)–C(3) 2.00(1), Cu(4)–C(5) 2.11(1), Cu(4)–C(6) 2.11(1), C(1)–C(2) 1.25(2), C(3)–C(4) 1.25(2), C(5)–C(6) 1.22(2); Cu(1)–C(1)–C(2) 139(1), Cu(1)–C(3)–C(4) 141(1), Cu(1)–C(5)–C(6) 143(1), C(1)–C(2)–C(7) 162(1), C(3)–C(4)–C(14) 163(1), C(5)–C(6)–C(21) 165(1), Cu(1)–C(1)–Cu(2) 70.0(4), Cu(1)–C(1)–Cu(3) 72.5(4), Cu(2)–C(1)–Cu(3) 135.4(7), Cu(1)–C(3)–Cu(3) 71.6(4), Cu(1)–C(3)–Cu(4) 73.9(4), Cu(3)–C(3)–Cu(4) 134.4(7), Cu(1)–C(5)–Cu(2) 72.0(4), Cu(1)–C(5)–Cu(4) 71.2(4), Cu(2)–C(5)–Cu(4) 135.8(7).

Table 1 Rate constants for the quenching of **1** by pyridinium acceptors in acetone (0.1 mol dm^{-3} $NBu^n_4PF_6$) at 25 °C

Quencher[a]	$E(A^{+/0})^b$/V *vs.* SSCE	k_q/ dm^3 mol^{-1} s^{-1}	$k_q'^c$/ dm^3 mol^{-1} s^{-1}	ln k_q'
4-Cyano-*N*-methylpyridinium	−0.67	4.68×10^9	8.80×10^9	22.90
4-Methoxycarbonyl-*N*-methylpyridinium	−0.78	3.53×10^9	5.46×10^9	22.42
4-Aminoformyl-*N*-ethylpyridinium	−0.93	5.21×10^8	5.50×10^8	20.12
3-Aminoformyl-*N*-methylpyridinium	−1.14	1.53×10^8	1.55×10^8	18.86
N-Ethylpyridinium	−1.36	1.71×10^7	1.71×10^7	16.65
4-Methyl-*N*-methylpyridinium	−1.49	1.22×10^6	1.22×10^6	14.01

[a] All compounds are hexafluorophosphate salts. [b] Ref. 8. [c] See ref. 9; $1/k_q' = 1/k_q - 1/k_d$.

The phosphorescence of **1** is found to be quenched by a number of pyridinium acceptors *via* an outer-sphere electron-transfer process. The bimolecular quenching rate constants are summarized in Table 1. An excited-state reduction potential [$E°(\mathbf{1}^{2+/+*})$] of −1.71 V *vs.* saturated sodium chloride calomel electrode (SSCE) (λ = 1.36 eV) has been estimated through oxidative quenching studies with a series of pyridinium acceptors, indicative of the strong reductive nature of the excited state.

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Footnotes

† ^1H NMR (CD_2Cl_2), δ 3.70 (s, 9H, OMe), 6.37–6.47 (dd, 12H, C_6H_4), 7.14–7.38 (m, 60H, Ph). Positive FAB MS, *m/z* 1696 {M}$^+$. IR(Nujol) ν/cm^{-1}, 830 (s, P–F). Anal. Calc. for $C_{99}H_{81}Cu_4F_6O_3P_5 \cdot 0.5CH_2Cl_2$: C, 63.42; H, 4.35. Found: C, 63.42; H, 4.46%.

‡ *Crystal data* $C_{99}H_{81}Cu_4F_6O_3P_5 \cdot C_6H_{14}$; M_r = 1927.95, monoclinic, space group $P2_1/c$ (no. 14), a = 19.300(5), b = 17.754(3), c = 28.290(4) Å, β = 108.64(2)°, U = 9185(2) Å^3, Z = 4, D_c = 1.394 g cm^{-3}, μ(Mo-Kα) = 10.64 cm^{-1}, $F(000)$ = 3976, T = 298 K, Nonius-Enraf CAD4 diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The space group was determined from systematic absences and the structure was solved by direct methods and difference Fourier method and refined by full-matrix least squares using the software package TeXsan on a Silicon Graphic Indy computer. Of the non-H atoms, only the four Cu and five P and three O atoms were refined anisotropically and the C and F atoms were refined isotropically to give R = 0.073 and wR = 0.077 for 5819 reflections with $I > 3\sigma(I)$ with $w = 4F_o^2/\sigma^2(F^2)$, where $\sigma^2(F^2) = [\sigma^2(I) + (0.010F_o^2)^2]$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/183.

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