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Photophysics and photochemical reactivities of organocopper(I) complexes. Crystal structure of $[Cu_2(PPh_2Me)_4(\mu,\eta^1\text{-}C{\equiv}CPh)_2]$

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Dimeric $[Cu_2(PPh_2Me)_4(\mu,\eta^1\text{-}C{\equiv}CPh)_2]$ has been synthesized and crystallographically characterized; its photophysics together with those of other related organocopper(I) complexes, $[Cu_2\{2\text{-}C(SiMe_3)_2C_5H_4N\}_2]$ and $[\{Cu(C_6H_2Me_3\text{-}2,4,6)\}_5]$ have been studied and Stern–Volmer quenching data of the phosphorescent state of the pyridine complex with organic halides are suggestive of a charge-transfer mechanism with a high driving-force regime.

There has been a growing interest in the spectroscopic and structural studies of polynuclear metal complexes with d^{10}–d^{10} metal–metal interactions.[1–3] Recently, both tri- and tetra-nuclear copper(I) complexes have been shown by us[1b–e] and others[2a c,h] to be strongly luminescent with rich photophysical and photochemical behaviour. This together with the increasing interest and versatility of organocopper reagents in organic synthesis as well as the increasing structural information on this class of compounds have prompted us to investigate their photophysical and photochemical properties. Herein, we report the synthesis, photophysics and structural characterization of dinuclear $[Cu_2(PPh_2Me)_4(\mu,\eta^1\text{-}C{\equiv}CPh)_2]$ **1** and the luminescent behaviour of two related organocopper(I) species, $[Cu_2\{2\text{-}C(SiMe_3)_2C_5H_4N\}_2]$ **2**[4] and $[\{Cu(mes)\}_5]$ **3** (mes = mesityl).[5]

Reaction of $[Cu(C{\equiv}CPh)]_n$ with two equivalents of methyldiphenylphosphine in dichloromethane under an inert atmosphere of nitrogen, followed by recrystallization from CH_2Cl_2–*n*-hexane afforded **1** as yellow-green crystals in *ca.* 65% yield. Complex **1** gave satisfactory elemental analyses and has been characterized by ^1H NMR and IR spectroscopy† and X-ray crystallography.

Fig. 1 shows a perspective drawing of complex **1** with the atomic numbering.‡ The structure consists of a discrete dimeric unit in which the copper and the bridging carbon atoms form a strictly planar rhomboid array. Each copper atom in the molecule assumes a distorted-tetrahedral environment. Although there are vast numbers of such diamonds present in the literature,[7–9] examples of a d^{10}-alkynyl diamond are extremely rare.[10] The C≡C distance in **1** of 1.200(5) Å is typical of that found for a terminal carbon–carbon triple bond. The C(1)–C(2)–C(3) and C(1′)–C(2′)–C(3′) bond angles are close to linearity [177.7(4)°] and the interactions of C(2) and C(2′) with Cu and Cu′ are negligible (average Cu • • • C distance is 3.086 Å), suggestive of little to no metal–acetylide π interaction. Thus the acetylide should best be formulated as a μ,η^1 bridge. However, unlike other symmetric acetylide bridges,[9,11] the copper acetylide bridges are asymmetric, showing a remarkable bent orientation, as reflected by the Cu–C distance [2.011(3) Å for Cu–C(1), 2.210(4) Å for Cu′–C(1)] and the Cu–C(1)–C(2) angle [159.3(3)° for Cu–C(1)–C(2), 127.7(3)° for Cu′–C(1)–C(2)].

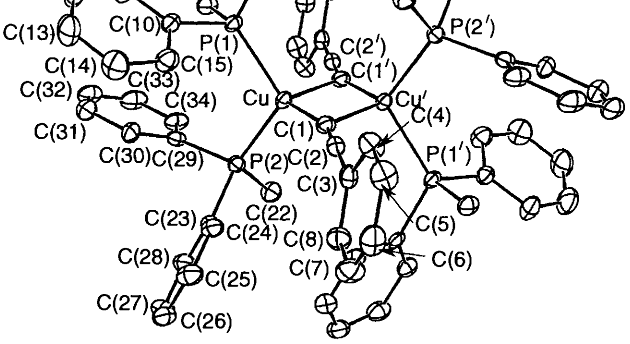
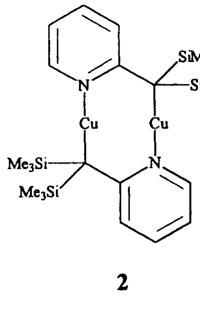


Fig. 1 Perspective drawing of $[Cu_2(PPh_2Me)_4(\mu,\eta^1\text{-}C{\equiv}CPh)_2]$ with the atomic numbering. Thermal ellipsoids are shown at the 30% probability level. The primed atoms have coordinates at (1 − *x*, 1 − *y*, −*z*). Selected bond distances (Å) and angles (°): Cu • • • Cu′ 2.454(1), Cu–P(1) 2.281(1), Cu–P(2) 2.2822(9), Cu–C(1) 2.011(3), C(1)–C(2) 1.200(5); Cu–C(1)–C(2) 159.3(3), Cu–C(1)–Cu′ 70.9(1), C(1)–Cu–C(1′) 109.1(1), C(1)–C(2)–C(3) 177.7(4), P(1)–Cu–P(2) 109.74(4), P(1)–Cu–C(1) 117.6(1), P(2)–Cu–C(1) 116.3(2)



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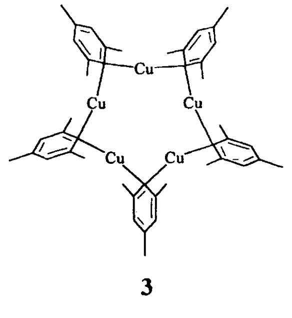

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† Complex **1** (Found: C, 72.15; H, 5.25. Calc. for $C_{68}H_{62}Cu_2P_4$: C, 72.25; H, 5.55%). ^1H NMR (CD_2Cl_2): δ 1.60 (s, 12 H, Me) and 6.50–7.50 (m, 50 H, Ph). IR (Nujol mull, KBr): 2032 [ν(C≡C)] cm^{-1}. UV/VIS (CH_2Cl_2), λ/nm ($\varepsilon_{max}/dm^3\ mol^{-1}\ cm^{-1}$): 248 (51 515) and 315 (15 290). Complex **2**. UV/VIS (*n*-hexane), λ/nm ($\varepsilon_{max}/dm^3\ mol^{-1}\ cm^{-1}$): 255 (32 085), 307 (6905) and 327 (sh) (2215).

‡ *Crystal data*. **1**, $C_{68}H_{62}Cu_2P_4$, $M_r = 1130.23$, triclinic, space group $P\bar{1}$, crystal dimensions 0.20 × 0.10 × 0.20 mm, $a = 11.168(2)$, $b = 11.587(2)$, $c = 12.496(2)$ Å, $\alpha = 88.14(2)$, $\beta = 64.72(1)$, $\gamma = 83.29(1)°$, $U = 1451.9(1.0)$ Å^3, $Z = 1$, $D_c = 1.293\ g\,cm^{-3}$, $\mu(Mo\text{-}K\alpha) = 8.81\ cm^{-1}$, $F(000) = 588$, $T = 295$ K, 334 parameters, $R = 0.035$ and $wR = 0.043$ for 2918 reflections with $I > 3\sigma(I)$ and with $w = 4F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.04F_o^2)^2]$. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.710 73 Å). The centric space group was confirmed by the successful solution and refinement of the structure solved by Patterson and Fourier methods and refined by full-matrix least squares on *F* using the Enraf-Nonius SDP Programs[6] on a MicroVax II computer. Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/145.

The Cu–Cu′ distance of 2.454(1) Å, which is shorter than the separation found in metallic copper (2.56 Å), is not uncommon in organocopper systems,[10] and may be suggestive of some weak bonding interaction between the two copper(I) centres. Short Cu • • • Cu contacts have also been observed in complexes **2** [2.412(1) Å][4a] and **3** [2.437(8)–2.469(9) Å].[5b]

The electronic absorption spectrum of complex **1** in dichloromethane shows a strong absorption band at *ca.* 248 nm, with a shoulder at *ca.* 315 nm and an absorption tail to longer wavelengths. Similarly, the electronic absorption spectrum of complex **2** in *n*-hexane is dominated by an absorption band centred at 255 nm, with shoulders at *ca.* 307 and 327 nm. For the free pyridine, 2-HC(SiMe$_3$)$_2$C$_5$H$_4$N, an absorption band occurs at *ca.* 270 nm and no absorption is seen at wavelengths longer than 300 nm.

Excitation of solid or fluid solutions of complexes **1**–**3** at $\lambda > 350$ nm produced long-lived, intense luminescence. The photophysical data are summarized in Table 1. The solid-state emission spectrum of complex **1** at room temperature shows a sharp peak situated at 467 nm and a shoulder to longer wavelength at 509 nm. Upon cooling to 77 K, the emission spectrum became vibronically structured, with vibrational progressions of *ca.* 1982 cm^{-1}, comparable to the ν(C≡C) stretch observed in the IR spectrum (2032 cm^{-1}). This is strongly suggestive of an emissive state involving the participation of the acetylide moiety. With reference to our previous spectroscopic work on copper(I) acetylide complexes,[1b] it is likely that the long-lived emission in **1** is derived from triplet states involving a ligand-to-metal charge-transfer (l.m.c.t.) (PhC≡C$^-$→Cu$_2$) character modified by metal–metal interactions. On the other hand, both the room-temperature and 77 K solid-state emission spectra of complexes **2** and **3** show a structureless emission band at *ca.* 520–550 nm and *ca.* 650 nm, respectively. The measured luminescence lifetimes of complexes **1** and **2** in the microsecond range are also indicative of emissive states of triplet parentage. Similarly, given the short Cu • • • Cu distances in complexes **2** and **3**, it is likely that the emissive states are derived from metal-centred d→s of Cu^I modified by copper–copper interactions. Emissions at similar energy have also been reported for Cu$^+$ ions in SiO$_2$ glass and Cu$^+$-doped Na$^+$-β″-alumina single crystals.[12] As for complex **1**, an assignment of the origin as l.m.c.t. modified by copper–copper interactions (R$^-$→Cu$_2$ in **2** and mes$^-$→Cu$_5$ in **3**) should not be overlooked owing to the strong σ-donor ability of the alkyl and aryl groups. The lower emission energy observed in **3** compared with **1** and **2** is in line with the increased extent of delocalization upon increasing the number of copper atoms, which causes a narrowing of the highest-occupied to the lowest-unoccupied molecular-orbital energy gap.

The phosphorescent state of complex **2** is found to be quenched by halogenocarbons. A correlation of the bimolecular-quenching rate constants with the half-wave reduction potentials [$E_{\frac{1}{2}}$(RX)] and carbon–halogen bond-dissociation energies [D(C–X)] of a series of halogenocarbons has been summarized in Table 2. The larger quenching rate constants for CCl$_4$ and CHCl$_3$ compared with CBr$_4$ and allyl bromide, which parallel the reduction potential of the halogenocarbons, are suggestive of an initial charge-transfer mechanism involving outer-sphere electron transfer as the rate-determining step with little dependence on the carbon–halogen bond-dissociation energy, *i.e.* $\mathrm{RX} + \mathrm{Cu_2}^* \rightleftharpoons [\mathrm{RX}, \mathrm{Cu_2}^*] \rightleftharpoons [\mathrm{RX}^{\bullet-}, {}^+\mathrm{Cu_2}]$. However, as the reduction potential of the halogenocarbons becomes increasingly negative, the trend becomes less well defined and the quenching rate constant for *n*-butyl bromide represents an anomaly, which could not be explained by using a simple outer-sphere model. With the excited-state reduction potential of complex **2**, $E^\circ(\mathbf{2}^+/\mathbf{2}^*)$ −1.6(1) V *vs.* SCE, estimated from a knowledge of its ground-state reduction potential [$E^\circ(\mathbf{2}^+/\mathbf{2}) = +0.76$ V *vs.* SCE] and zero spectroscopic energy [$E_{0\ 0} \approx 2.4(1)$ eV, eV $\approx 1.60 \times 10^{-19}$ J], it is likely that given the very negative reduction potential of *n*-butyl bromide, the quenching by an outer-sphere process becomes inaccessible or so slow that the quenching mechanism is taken over by an initial inner-sphere process in which the formation of a M–X bond and the rupture of the R–X bond occur simultaneously, the rate constant of which would be dependent upon the carbon–halogen bond-dissociation energies, $\mathrm{RX} + \mathrm{Cu_2}^* \rightleftharpoons [\mathrm{RX} \cdots \mathrm{Cu_2}^*] \rightleftharpoons [\mathrm{R} \cdots \mathrm{X} \cdots \mathrm{Cu_2}]$. It is likely that the outer-sphere process is favoured by halogenocarbons with less negative reduction potentials while the inner-sphere process is important for those of more negative reduction potentials and small carbon–halogen bond-dissociation energies. Nevertheless, the two models described are extreme cases and the reaction of complex **2** with RX may involve a mechanism intermediate between the two.

Table 1 Photophysical data for complexes **1**–**3**

Complex	Medium (T/K)[a]	λ_{em}/nm (τ_0/μs)
1	Solid (298)	467, 509 (87 ± 5)
	Solid (77)	464, 511
	CH$_2$Cl$_2$ (298)[b]	529, 660 (sh)
2	Solid (298)	520 (12 ± 1)
	Solid (77)	551, 520 (sh)
	n-Hexane (298)[c]	515 (6.8 ± 0.6)
	Tetrahydrofuran (298)[c]	534 (6.0 ± 0.6)
3	Solid (298)	644
	Solid (77)	653

[a] All solutions were degassed by at least four freeze–pump–thaw cycles. [b] [Cu$_2$] ≈ 0.2 mmol dm^{-3}. [c] [Cu$_2$] ≈ 0.02 mmol dm^{-3}.

Table 2 Rate constants for the quenching reaction of [Cu$_2${2-C(SiMe$_3$)$_2$C$_5$H$_4$N}$_2$]* by halogenocarbons in degassed *n*-hexane at 298 K

Quencher	$E_{\frac{1}{2}}$(RX/RX$^{\bullet-}$)[a]/V	D(C–X)[b]/ kcal mol^{-1}	k_q/dm^3 mol^{-1} s^{-1}
CBr$_4$	−0.30	56	2.16×10^{10}
CCl$_4$	−0.78	70	3.06×10^{9}
CH$_2$=CHBr	−1.21	55	3.87×10^{6}
CHCl$_3$	−1.67	78	2.04×10^{6}
PhCH$_2$Cl	−1.94	—	4.45×10^{5}
Bu^{n}Br	−2.27	69	6.79×10^{6}

[a] *vs.* saturated calomel electrode (SCE). From ref. 13. [b] cal = 4.184 J. From ref. 14.

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