Synthesis, structure, photophysics, time-resolved emission spectroscopy and electrochemistry of luminescent copper(I) acetylide complexes

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A series of soluble trinuclear copper(I) complexes containing mono- and bi-capped μ_3-η^1-acetylides [Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CR)]$^{2+}$ and [Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CR)$_2$]$^+$ (dppm = Ph$_2$PCH$_2$PPh$_2$, R = Ph or Bu^t) have been synthesized and shown to exhibit long-lived dual luminescent behaviour. Their photophysics and electrochemistry and those of a mixed halide–acetylide capped trinuclear copper(I) complex [Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CBu^t)(μ_3-Cl)]$^+$ have been investigated. The origin of the low-energy emission (λ_{em} 525–700 nm) is ascribed to states of ds/l.m.c.t. admixture with large l.m.c.t. (ligand to metal charge transfer) character. The crystal structure of [Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CBu^t)][PF$_6$]$_2$ has been determined. The complex consists of an isosceles triangular array of copper atoms with Cu–Cu distances of 2.910(1), 2.941(2) and 3.175(1) Å.

The growing interest in the synthesis of alkynylmetal complexes owing to recent reports on their potential applications as non-linear optical materials and molecular wires[1] and the wide variety of possible bonding modes of the alkynyl moiety has encouraged us to investigate their potential in polynuclear metal complex formation. In view of this and our continuing efforts and interests in the photophysics and photochemistry of polynuclear metal complexes,[2] a program to study the photophysics and reactivities of a series of soluble polynuclear metal acetylides was launched.[2b–e] Polynuclear d^{10} metal complexes have been shown to display rich photo-physical and -chemical behaviour.[2,3] Prominent examples include halide clusters such as [Cu$_4$I$_4$(py)$_4$] (py = pyridine), [Cu$_4$I$_4$-(PPh$_3$)$_4$],[3a,b] and [Ag$_4$I$_4$(PPh$_3$)$_4$];[3d] some of which have been shown to exhibit interesting 'luminescence thermochromism' and dual luminescence properties. Trinuclear copper(I) complexes containing capped μ_3-η^1-acetylides have been synthesized by Gimeno and co-workers[4,5] and us;[2b] the structures of some of them have also been determined. The close resemblance of the acetylide moiety to the halide ion in a variety of aspects has prompted us to investigate the photoluminescent properties of this class of compounds. Recently we showed that these complexes exhibit rich photoluminescent behaviour;[2b] their long-lived phosphorescent states are capable of acting as strong reducing agents.[2c] In this paper, the synthesis, photophysics, time-resolved emission spectroscopy, photochemistry and electrochemistry of trinuclear copper(I) monocapped acetylide analogues will be described; the crystal structure of [Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CBu^t)][PF$_6$]$_2$ (dppm = Ph$_2$PCH$_2$-PPh$_2$) will also be reported.

Experimental

Materials

Bis(diphenylphosphino)methane (dppm) was obtained from Strem Chemicals. The complex [Cu$_2$(dppm)$_2$(MeCN)$_2$][PF$_6$]$_2$ was prepared by a literature procedure.[6] Phenylacetylene and 3,3-dimethylbut-1-yne were obtained from Aldrich Chemical Co. Tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte for photophysical, photochemical and electrochemical studies was obtained from Aldrich and recrystallized twice from absolute ethanol before use. All solvents were purified and distilled using standard procedures before use.[7] All other reagents were of analytical grade and were used as received.

Synthesis of copper complexes

All reactions were carried out under anaerobic and anhydrous conditions using standard Schlenk techniques; the syntheses of complexes 3–5 have previously been communicated.[2b]

[Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CPh)][BF$_4$]$_2$ 1. This complex was prepared by the literature method.[4a] UV/VIS (MeCN): λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 260 (sh) (41 450) and 330 (sh) (14 290).

[Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CBu^t)][PF$_6$]$_2$ 2. A solution of the complex [Cu$_2$(dppm)$_2$(MeCN)$_2$][PF$_6$]$_2$ (127 mg, 0.10 mmol) in acetone (25 cm^3) was treated dropwise with Bu^{t}C≡CLi (0.11 mmol) prepared from 3,3-dimethylbut-1-yne (0.11 mmol) and LiBu^n (0.11 mmol) and stirred at room temperature for 24 h to give a colourless solution. After evaporation to dryness, the resulting solid was extracted with acetone (3 × 8 cm^3), and the solution was filtered and reduced in volume. Subsequent precipitation by addition of diethyl ether gave complex 2 as an air-stable yellow solid. It was washed with absolute ethanol, redissolved in acetone, filtered, and subsequent diffusion of diethyl ether gave 2 as air-stable yellow crystals (yield 67 mg, 40%) {Found: C, 57.2; H, 4.4. Calc. for [Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CBu^t)][PF$_6$]$_2$·Me$_2$CO: C, 56.9; H, 4.6%}. NMR [(CD$_3$)$_2$CO]: ^{1}H, δ 1.29 (s, 9 H, Bu^t), 3.83 (s, br, 6 H, CH$_2$) and 7.1–7.5 (m, 60 H, Ph); ^{31}P, δ −8.24. IR (Nujol mull, KBr): 839 cm^{-1} [v(P–F)]. UV/VIS (MeCN): λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 260 (sh) (40 890) and 330 (sh) (2120).

The following complexes were prepared as previously described: [Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CPh)$_2$]PF$_6$ 3[2b,4b] UV/VIS (MeCN) λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 255 (sh) (48 825) and 305 (sh) (32 390); [Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CBu^t)$_2$]PF$_6$ 4,[2b] UV/VIS (MeCN) λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 255 (sh) (39 280) and 350 (sh) (6150); and [Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CBu^t)(μ_3-Cl)]PF$_6$ 5,[2b] UV/VIS (MeCN) λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}) 255 (sh) (42 170) and 330 (sh) (6950).

Physical measurements and instrumentation

The UV/VIS spectra were obtained on a Milton Roy Spectronic 3000 diode-array spectrophotometer, IR spectra as Nujol mulls on a Shimadzu IR-470 spectrophotometer (4000–400 cm^{-1}), and steady-state excitation and emission spectra on a Spex Fluorolog-2 111 spectrofluorometer equipped with a Hamamatsu R928 photomultiplier. Low-temperature (77 K) spectra were recorded from glass matrices by using a quartz optical

Dewar sample holder. Proton and ^{31}P NMR spectra were recorded on a JEOL JNM-GSX270 Fourier-transform spectrometer with chemical shifts reported relative to $SiMe_4$ and H_3PO_4, respectively. Elemental analyses of the new complexes were performed by Butterworth Laboratories Ltd.

Emission-lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Quanta-Ray GCR-150 pulsed Nd-YAG laser. Luminescence decay signals were recorded on a Tektronix TDS 620A digital oscilloscope interfaced to an IBM personal computer for data acquisition and analysis using a program for exponential fits. Time-resolved emission spectroscopy was performed by time-correlated single-photon counting. Laser excitation at 300 nm was provided by the frequency-doubled output of a rhodamine 6G dye laser (Coherent 590), synchronously pumped by a mode-locked Coherent Antares 76-S Nd-YAG laser. This gave UV light with an average power of less than 0.5 mW and pulse widths of approximately 10 ps. Emission was imaged through a magic angle polarizer onto the slits of a Spex 1680B 0.22 m negative-dispersion monochromator and detected with a Hamamatsu R928 photomultiplier tube.

Transient difference absorption spectroscopy was performed by using the 355 nm output of a Quanta-Ray GCR-150 pulsed Nd-YAG laser as the excitation source of the flash-photolysis set-up. The transient species were generated by the laser pulse and their absorption was monitored by a 250 W Oriel quartz–tungsten–halogen lamp oriented orthogonal to the direction of the laser pulse. The output of the lamp was wavelength selected by passing through two monochromators (Oriel 77250, 1/8 m and 77200, 1/4 m) and detected by a Hamamatsu R928 photomultiplier tube. The signal from the latter was amplified using a Tektronix AM 502 differential amplifier and recorded on a Tektronix TDS 620A digital oscilloscope interfaced to an IBM personal computer for data acquisition and analysis.

All solutions for photophysical and photochemical studies were prepared under vacuum in a round-bottom flask (10 cm^3) equipped with a side-arm fluorescence cuvette (1 cm) and sealed from the atmosphere by a Kontes quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze–pump–thaw cycles.

Cyclic voltammetric measurements were performed by using a Princeton Applied Research (PAR) potentiostat/galvanostat (model 273). The ferrocenium–ferrocene couple was used as the internal standard in the electrochemical measurements in acetonitrile (0.1 mol dm^{-3} NBu$^n_4$PF$_6$). The working electrode was a glassy carbon (Atomergic Chemetals V25) electrode with platinum foil acting as the counter electrode. The electrode surfaces were treated as reported elsewhere.[8]

Crystallography

A crystal of complex **2** was obtained by vapour diffusion of diethyl ether into acetone.

Crystal data. $C_{81}H_{75}Cu_3F_{12}P_8$, $M_r = 1714.89$, triclinic, space group $P\bar{1}$ (no. 2), $a = 13.952(2)$, $b = 14.130(4)$, $c = 20.432(3)$ Å, $\alpha = 92.05(1)$, $\beta = 92.57(1)$, $\gamma = 100.49(2)°$, $U = 3952.7(1.0)$ Å^3, $Z = 2$, $D_c = 1.441$ g cm^{-3}, $\mu(Mo-K\alpha) = 10.31$ cm^{-1}, $F(000) = 1752$.

A crystal of dimensions $0.15 \times 0.2 \times 0.25$ mm was used for data collection at 23 °C on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.710\ 73$ Å) using ω–2θ scans with ω-scan angles $(0.60 + 0.344\ \tan\ \theta)°$ at speeds of 1.18–8.24° min^{-1}. Intensity data, measured in the ranges $2\theta_{max} = 44°$; h, 0–14; k, −14 to 14 and l, −21 to 21, were corrected for Lorentz-polarization effects and empirical absorption based on ψ scans of five strong reflections (minimum and maximum transmission factors 0.842

and 0.999). A total of 10 768 reflections were collected, 9752 of which were measured once and 704 twice ($R_{merge} = 0.027$), giving 10 260 independent reflections.

Structure determination and refinement. The centric space group was confirmed by the successful solution of the structure by Patterson and Fourier methods and refined by full-matrix least squares with atomic scattering factors taken from ref. 9. Calculations were carried out on a Micro Vax II computer using the SDP program.[10] The crystallographic asymmetric unit consists of 3 Cu, 6 P, 81 C and 75 H atoms of the complex divalent cation, one PF$_6^-$ anion, and two half PF$_6^-$ anions with the two P atoms at special positions. The Cu and P atoms of the cluster and the P and F atoms of the anions were refined anisotropically, the 81 C isotropically and 75 H atoms at calculated positions and with isotropic thermal parameters equal to 1.3 times that of the attached C atom were not refined. Convergence for 535 variables by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.05F_o^2)^2]$ for reflections with $I \geqslant 3\sigma(I)$, was reached at $R = 0.069$, $R' = 0.089$ and $S = 2.372$ for the 6685 reflections with $F_o \geqslant 6\sigma(F_o)$; $(\Delta/\sigma)_{max} = 0.02$ for atoms of the complex cation. The thermal parameters of the two half anions differ markedly, with those of atoms P(9) and F(10)–F(12) significantly higher than those of P(8) and F(7)–F(9). The last four atoms have thermal parameters comparable to those of the other PF$_6^-$ anion. However, there was no evidence of disorder in any of the PF$_6^-$ anions. The crystal structure having twelve phenyl rings radiating out from the core must have an interfering effect in the scattering process and many of the resultant diffraction beams were rather weak. A final Fourier-difference map was featureless, with maximum positive and negative peaks of 0.89 and 0.75 e Å^{-3}, respectively. Selected bond distances and angles are listed in Table 1.

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 186/133.

Results and Discussion

Complexes **1** and **3** were prepared according to the literature methods;[4] **2**, **4** and **5** have also been synthesized, of which **2** and **5**[2b] have been characterized by X-ray crystallography. An independent report on the preparation of **2**, **4** and **5** has been published by Gimeno and co-workers.[5]

A perspective drawing of the crystal structure of complex **2** with atomic numbering is depicted in Fig. 1. The complex consists of an isosceles triangular array of copper atoms with a dppm ligand bridging each edge to form a roughly planar [Cu$_3$P$_6$]$^+$ core. The bridging mode of the alkynyl group is asymmetric with the Cu–C bond distances in the range 1.997(9)–2.067(8) Å and the bond angles between the alkynyl group and each copper atom [Cu–C(1)–C(2)] in the range 107.9(6)–134.7(8)°. The linearity of the *tert*-butylacetylide group [C(1)–C(2)–C(3) 177(2)°] and the C≡C bond distance [1.23(1) Å] are characteristic of metal–acetylide σ bonding. A similar bonding mode has been found in the analogous complexes **1**,[4a,5] **3**[5] and **5**.[2b]

The electronic absorption spectra of complexes **1**–**5** in MeCN exhibit intense low-energy bands in the 300–350 nm region. Excitation of solid samples or fluid solutions of **1**–**5** at $\lambda > 350$ nm produced long-lived intense dual luminescence. The photophysical data are collected in Table 2. Fig. 2 shows the time-resolved emission spectra of **5** in degassed MeCN at two different time windows. Similar results have been obtained for the other complexes. The low-temperature (77 K) solid-state emission spectra of complexes **1**–**5** showed very similar patterns,
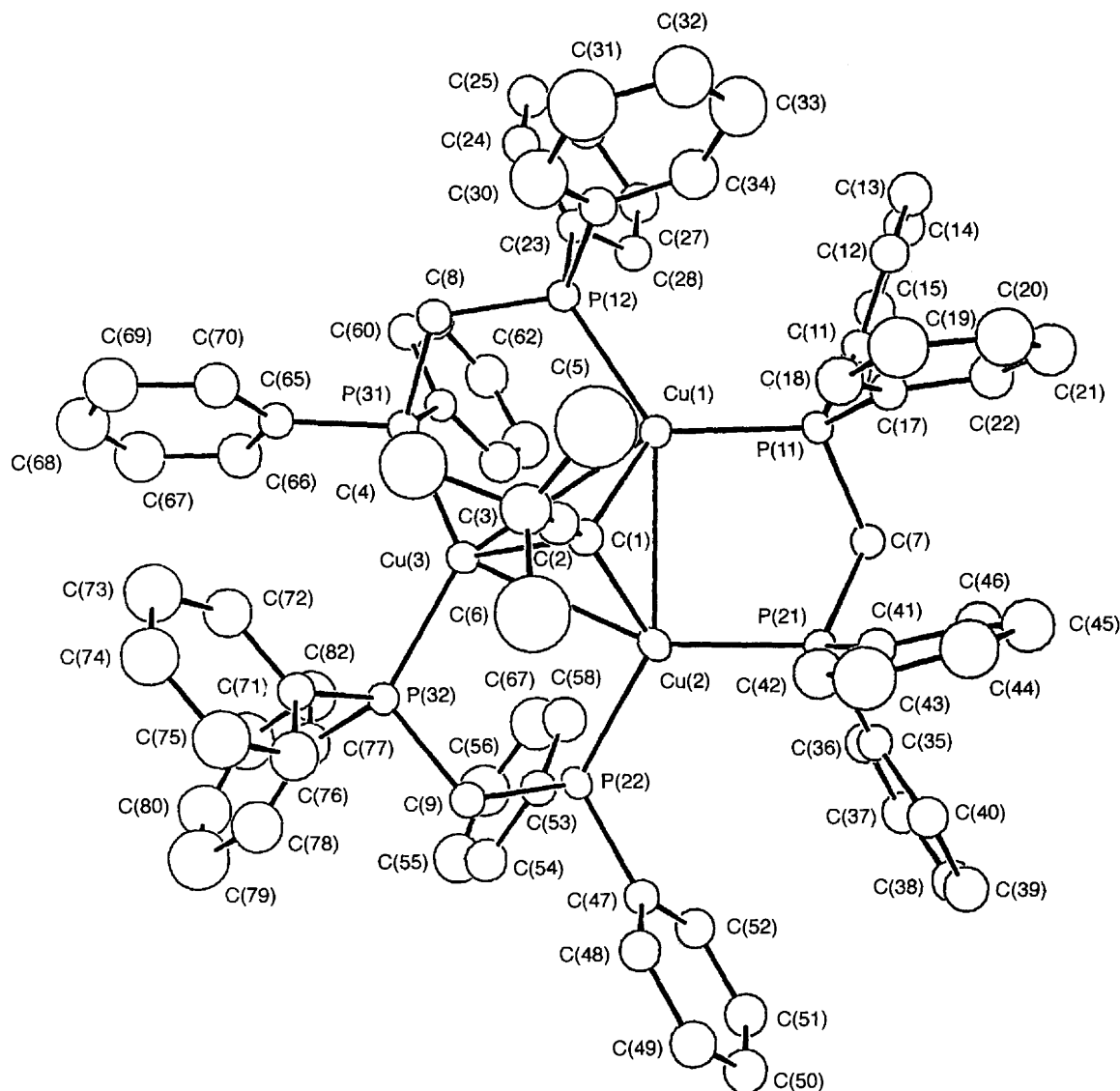
Fig. 1 Perspective drawing of the [Cu₃(dppm)₃(C≡CBuᵗ)]²⁺ cation showing thermal ellipsoids at the 25% probability level and the numbering scheme

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for compound 2

Cu(1)–Cu(2)	2.941(2)	Cu(1)–Cu(3)	3.175(1)
Cu(2)–Cu(3)	2.910(1)	Cu(1)–C(1)	2.050(9)
Cu(2)–C(1)	1.997(9)	Cu(3)–C(1)	2.067(8)
C(1)–C(2)	1.23(1)		
Cu(1)–Cu(2)–Cu(3)	65.74(4)	Cu(1)–Cu(3)–Cu(2)	57.60(3)
Cu(2)–Cu(1)–Cu(3)	56.67(3)	Cu(1)–C(1)–Cu(2)	93.2(3)
Cu(1)–C(1)–Cu(3)	100.9(4)	Cu(2)–C(1)–Cu(3)	91.4(3)
C(1)–C(2)–C(3)	177(2)		

Fig. 2 Time-resolved emission spectra of [Cu₃(dppm)₃(C≡CBuᵗ)-Cl]PF₆ in degassed acetonitrile. The peak at 600 nm is due to laser scattering

a high-energy band at *ca.* 440–495 nm and a lower-energy emission at *ca.* 525–700 nm. The high-energy emission is likely to be due to either metal to ligand charge transfer [Cu→π*(RC≡C⁻) m.l.c.t.] or intraligand [π→π*(RC≡C⁻) i.l.] in nature since complexes 2, 4 and 5 emit at similar energies (450 nm for 2 and 4, 440 nm for 5) while emission of 1 and 3 occurs at lower energy (492 nm for 1 and 485 nm for 3), consistent with the lower π* energy level for the phenylacetylide moiety. The low-energy emission is most likely associated with a spin-forbidden transition given the long lifetime observed. It is likely that the low-energy emitting state is related to the metal-centred excited state 3d⁹4s¹ of Cuᴵ modified by the copper–copper
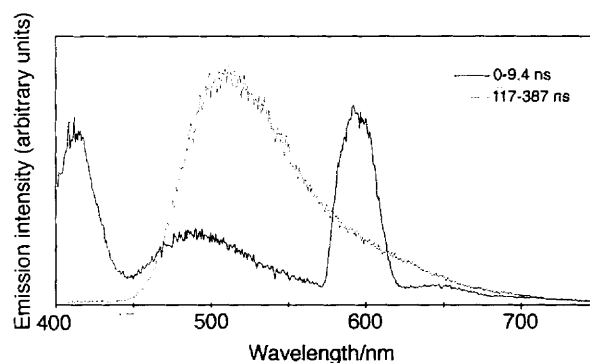
interaction due to configuration mixing of the filled orbitals of d parentage with appropriate empty orbitals derived from the higher-energy 4s and 4p atomic orbitals of the trimeric copper unit (d→s). Another possible assignment would be an acetylide to metal charge-transfer (RC≡C⁻→Cu₃ l.m.c.t.) excited state. Similar assignments have been suggested for the tetrameric iodocopper(I) clusters.³ᵇ In this context, we believe that with complexes 2, 4 and 5, where the strongly σ-donating BuᵗC≡C⁻ is involved, the low-energy emission is likely to derive from

Compound	Medium (T/K)	λ_{em}/nm(τ_o/μs)
1	Solid (298)	500 (21 ± 2)
	Solid (77)	492, 530 (sh)
	Me$_2$CO (298)	499 (6.8 ± 0.7)*
	MeCN (298)	499 (15 ± 1)*
2	Solid (298)	627 (14 ± 1)
	Solid (77)	450, 570 (sh), 692
	Me$_2$CO (298)	640 (2.6 ± 0.3)*
3	Solid (298)	493 (14 ± 1)
	Solid (77)	485, 525 (sh)
	Pr^{n}CN glass (77)	471, 500 (sh)
	Me$_2$CO (298)	495 (5.9 ± 0.5)*
	MeCN (298)	494 (6.5 ± 0.6)*
4	Solid (298)	450 (0.44 ± 0.05)
		540 (1.7 ± 0.2)
	Solid (77)	450, 530 (sh)
	Pr^{n}CN glass (77)	442, 500 (sh)
	Me$_2$CO (298)	444 (0.24 ± 0.02)*
		580 (sh) (16 ± 1)*
	MeCN (298)	456 (0.27 ± 0.03)*
		600 (sh) (4.1 ± 0.4)*
5	Solid (298)	440 (sh) (<0.01)
		535 (33 ± 3)
	Solid (77)	440, 572
	MeCN (298)	540 (sh) (5.3 ± 0.5)*
		613 (5.4 ± 0.5)*

* [Cu$_3$] $\approx$ 0.2 mmol dm^{-3}.

Compound	d(Cu–Cu)/Å	Ref.
1	2.813(3)–3.274(3)	4(a), 5
2	2.910(1)–3.175(1)	This work
3	2.570(3)–2.615(3)	4(b), 5
5	2.754(2)–2.927(2)	2(b)

Table 4 Rate constants for the quenching of [Cu$_3$(dppm)$_3$-(C≡CBu^t)]$^{2+}$* by pyridinium acceptors in degassed acetone (0.1 mol dm^{-3} NBu$^n_4$PF$_6$) at 25 °C

Quencher	E(A$^{+/0}$)/V $vs.$ SSCE*	k_q/dm^3 mol^{-1} s^{-1}
3,4-Dicyano-N-methylpyridinium tetrafluoroborate	−0.13	6.89 × 10^8
2-Chloro-N-methyl-3-nitropyridinium tetrafluoroborate	−0.39	5.18 × 10^7
4-Cyano-N-methylpyridinium hexafluorophosphate	−0.67	1.67 × 10^7
4-Methoxycarbonyl-N-methylpyridinium hexafluorophosphate	−0.78	< 10^6

* Ref. 13.

Fig. 3 Transient absorption difference spectrum recorded 10 μs after laser flash excitation of [Cu$_3$(dppm)$_3$(C≡CBu^t)]$^{2+}$ (3.95 × 10^{-5} mol dm^{-3}) and 4-methoxycarbonyl-N-methylpyridinium (0.027 mol dm^{-3}) in degassed acetone (0.1 mol dm^{-3} NBu$^n_4$PF$_6$)

states of ds/l.m.c.t. admixture with predominantly l.m.c.t. character. This is based on the following experimental findings. First, this low-energy emission band shows solvatochromism with its energy shifted to the blue on going from acetonitrile to the less-polar solvent acetone, indicative of its charge-transfer nature.[11] Secondly, the band of **2** is red shifted relative to those of **4** and **5**. This is consistent with the fact that **2** carrying an overall charge of 2 + would render the metal centre more readily reducible. A pure ds origin would predict **2** to emit at higher energy owing to the larger Cu–Cu distances in the monocapped system relative to the mixed halide–acetylide capped and bicapped systems (Table 3). The red shift for **2** is also in accord with that expected for an l.m.c.t. assignment with decreasing co-ordination number.[11] For complexes **1** and **3** the low-energy emission is also likely to derive from states of ds/l.m.c.t. admixture. However, the red shift in energy expected on going from **3** to **1** is indiscernible. This could either be a result of masking of the low-energy band by the intense high-energy emission which renders the location of the low-energy band maximum difficult, or a reduced l.m.c.t. contribution to the ds/l.m.c.t. admixture in the case of the less electron-donating phenylacetylide. The latter explanation would assume a state predominantly of ds origin. Similar d→s energies (λ_{em} $\approx$ 540 nm) have also been observed in other copper(I) systems.[12]

The phosphorescent state of [Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CBu^t)][PF$_6$]$_2$ was found to be quenched by a number of pyridinium acceptors. The quenching rate constants, as well as the reduction potentials of the pyridinium salts, are summarized in Table 4. Since the triplet-state energy of pyridinium ion is too high for any appreciable energy-transfer reaction between the excited state of the complex and the quencher, the quenching mechanism is most likely electron transfer in nature. This was confirmed by nanosecond transient absorption spectroscopy. Laser flash photolysis of a degassed acetone solution (0.1 mol dm^{-3} NBu$^n_4$PF$_6$) of [Cu$_3$(dppm)$_3$(μ_3-η^1-C≡CBu^t)][PF$_6$]$_2$ (3.95 × 10^{-5} mol dm^{-3}) and 4-methoxycarbonyl-N-methylpyridinium hexafluorophosphate (0.027 mol dm^{-3}) generated a transient absorption difference spectrum as illustrated in Fig. 3. The spectrum was recorded 10 μs after the laser flash. It is dominated by two bands: one at ca. 400 nm and a much broader peak at ca. 850 nm. The first band is characteristic
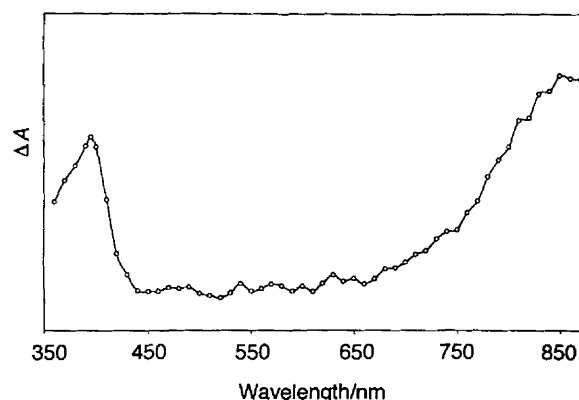
of pyridinyl radical and matched well with the literature spectrum of the reduced radical of 4-methoxycarbonyl-N-methylpyridinium.[14] On the other hand, the second band could not arise from the pyridinyl radical. Evidence was provided from an independent laser flash-photolysis study of [Au$_3$-(dmmp)$_2$][ClO$_4$]$_3$ [dmmp = bis(dimethylphosphinomethyl)-methylphosphine] and 4-methoxycarbonyl-N-methylpyridinium ion using the same instrumental set-up. This complex is a strong reducing agent in its excited state, as revealed by its excited-state redox potential E[Au$_3$(dmmp)$_2$]$^{4+/3+}$*, estimated to be −1.6(1) V $vs.$ saturated sodium chloride calomel electrode (SSCE).[2g] The phosphorescent state of [Au$_3$(dmmp)$_2$]$^{3+}$* undergoes facile electron-transfer quenching with 4-methoxycarbonyl-N-methylpyridinium ion in acetonitrile (0.1 mol dm^{-3} NBu$^n_4$PF$_6$) with a rate constant of 2.32 × 10^9 dm^3 mol^{-1} s^{-1}. The transient absorption difference spectrum recorded 35 μs after laser flash photolysis of a degassed acetonitrile solution (0.1 mol dm^{-3} NBu$^n_4$PF$_6$) of [Au$_3$(dmmp)$_2$]$^{3+}$ (2.2 × 10^{-4} mol dm^{-3}) and 4-methoxycarbonyl-N-methylpyridinium ion (0.014 mol dm^{-3}) at room temperature was characterized by a strong absorption band at ca. 390 nm but no significant absorption around 800 nm. That is, neither the [Au$_3$(dmmp)$_2$]$^{4+}$ nor the reduced 4-methoxycarbonyl-N-methylpyridinyl radical absorbed in this region. This led to the conclusion that the band at 850 nm in Fig. 3 could not be due to the pyridinyl radical.
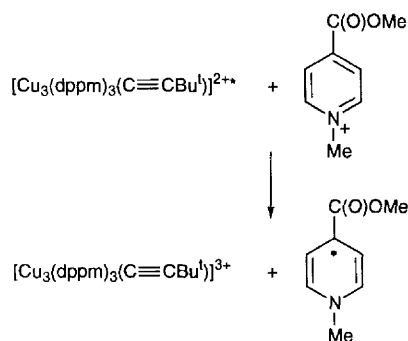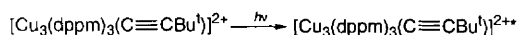
Scheme 1

The mechanism for the reaction of $[Cu_3(dppm)_3(C{\equiv}C\text{-}Bu^t)]^{2+*}$ and 4-methoxycarbonyl-N-methylpyridinium ion is likely to be as shown in Scheme 1. The band at 850 nm is probably a result of the mixed-valence $Cu^I Cu^I Cu^{II}$ species and can be attributed to an intervalence-transfer (i.t.) transition: $[Cu^I Cu^I Cu^{II}] \xrightarrow{h\nu} [Cu^I Cu^{II} Cu^I]^*$ Similar transient absorption bands have been observed for other copper(I)–acetylide systems.[2c]

The cyclic voltammograms of both complexes **1** and **2** in MeCN (0.1 mol dm^{-3} NBu$^n_4$PF$_6$) show a quasi-reversible oxidation couple at ca. $+0.38$ and $+0.36$ V, respectively, vs. ferrocenium–ferrocene assignable to one-electron oxidation at the Cu^I. Similar assignments have been suggested for complexes **3** and **4**.[2b] Further oxidation of these clusters resulted in decomposition, as evidenced by the irreversibility of the couples at more anodic potentials.

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