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Synthesis and photophysics of tetranuclear copper(I) acetylides. Crystal structure of $[Cu_4\{P(C_6H_4Me\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$

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A series of tetranuclear copper(I) acetylide complexes $[Cu_4(PR_3)_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$ (R = Ph **1**, C_6H_4F-*p* **2**, C_6H_4Me-*p* **3** or C_6H_4OMe-*p* **4**) have been synthesized and shown to exhibit rich photoluminescent behaviour at room temperature. The crystal structure of **3** has also been determined.

There has been a growing interest in polynuclear metal complexes, which have been shown by us and others to exhibit interesting and rich photoluminescent and structural properties.[1–3] An interesting example of polynuclear copper(I) clusters are the amine/pyridine (py) adducts of copper(I) halides, which were first reported by Hardt and co-workers.[4] The most extensively probed member of this series was $[Cu_4I_4(py)_4]$.[2a] An analogous $[Ag_4I_4(PPh_3)_4]$ cluster which exists both in the chair and cubane forms has also been reported to show interesting luminescent behaviour.[5] In view of the similarity of the halide and the acetylide moiety and our enormous efforts on the synthesis, photophysics and spectroscopic studies of acetylide-bridged polynuclear d^{10} and d^8 metal complexes,[1] a programme was initiated to synthesize the isostructural tetranuclear d^{10} metal clusters of acetylides. In this report the synthesis and photophysics of a series of $[Cu_4(PR_3)_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$ (R = aryl) compounds and the crystal structure of $[Cu_4\{P(C_6H_4Me\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$ will be described.

Experimental

Materials

Bis(diphenylphosphino)methane was obtained from Strem Chemicals, Inc.; $[Cu(MeCN)_4]X$[6] and $[\{Cu(C{\equiv}CPh)\}_n]$[7] were prepared by literature procedures. Phenylacetylene was obtained from Aldrich Chemical Co., tris(*p*-fluorophenyl)-, tris(*p*-methoxyphenyl)- and tris(*p*-tolyl)-phosphine from Strem Chemicals, Inc. All solvents were purified and distilled using standard procedures before use.[8] All other reagents were of analytical grade used as received.

Synthesis of copper complexes

All reactions were carried out under anaerobic and anhydrous conditions using standard Schlenk techniques.

$[Cu_4(PPh_3)_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$ 1. This was prepared by a method different from that previously reported by Naldini *et al.*[9] A mixture of $[Cu(MeCN)_4]PF_6$ (200 mg, 0.54 mmol), an excess of triphenylphosphine (600 mg, 2.30 mmol), phenylacetylene (51 mg, 0.54 mmol) and potassium hydroxide (30 mg, 0.54 mmol) in CH_2Cl_2–MeOH (3 : 1 v/v, 20 cm^3) was stirred at room temperature for 24 h. Addition of hexane to the yellow solution afforded complex **1** as air-stable yellow crystals. Yield: 165 mg (72%). UV/VIS (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 261 (71 300), 386 (17 150) and 445 (10 675). IR (Nujol mull, KBr): 2020 cm^{-1} [$\nu(C{\equiv}C)$] {Found: C, 73.20; H, 4.55. Calc. for $[Cu_4(PPh_3)_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$: C, 73.15; H, 4.75%}.

$[Cu_4\{P(C_6H_4F\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$ 2. A mixture of $[\{Cu(C{\equiv}CPh)\}_n]$ (99 mg, 0.60 mmol) and tris(*p*-fluorophenyl)phosphine (183 mg, 0.60 mmol) in dichloromethane was stirred at room temperature for 24 h. The yellow solution was filtered and addition of hexane afforded complex **2** as air-stable yellowish green crystals. Yield: 87 mg (30%). UV/VIS (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 260 (69 790), 310 (31 965) and 400 (7305). IR (Nujol mull, KBr): 2020 cm^{-1} [$\nu(C{\equiv}C)$]. ^1H NMR (CD_2Cl_2): δ 6.0–7.6 (m, Ph) (Found: C, 64.30; H, 3.50. Calc. for $[Cu_4\{P(C_6H_4F\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]\cdot H_2O$: C, 64.35; H, 3.65%).

$[Cu_4\{P(C_6H_4Me\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$ 3. The procedure was similar to that for the preparation of complex **2** except that tris(*p*-tolyl)phosphine was used in place of tris(*p*-fluorophenyl)phosphine. Recrystallization using CH_2Cl_2–hexane gave air-stable yellow crystals of **3**. Yield: 93 mg (33%). UV/VIS (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 260 (86 405), 320 (36 750) and 400 (7710). IR (Nujol mull, KBr): 2015 cm^{-1} [$\nu(C{\equiv}C)$]. ^1H NMR (CD_2Cl_2): δ 2.25 (s, 36 H, Me) and 5.93–7.50 (m, 68 H, Ph) (Found: C, 73.20; H, 5.30. Calc. for $[Cu_4\{P(C_6H_4Me\text{-}p)\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]\cdot H_2O$: C, 73.55; H, 5.65%).

$[Cu_4\{P(C_6H_4OMe\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$ 4. The procedure was similar to that for the preparation of complex **2** except that tris(*p*-methoxyphenyl)phosphine was used in place of tris(*p*-fluorophenyl)phosphine. Recrystallization using CH_2Cl_2–hexane gave air-stable yellow crystals of **4**. Yield: 80 mg (26%). UV/VIS (CH_2Cl_2), λ/nm (ε_{max}/dm^3 mol^{-1} cm^{-1}): 260 (133 210), 320 (41 210) and 400 (7735). IR (Nujol mull, KBr): 2018 cm^{-1} [$\nu(C{\equiv}C)$]. ^1H NMR (CD_2Cl_2): δ 3.67 (s, 36 H, OMe) and 6.06–7.57 (m, 68 H, Ph) (Found: C, 66.10; H, 4.70. Calc. for $[Cu_4\{P(C_6H_4OMe\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]\cdot 0.5\ CH_2Cl_2$: C, 66.30; H, 5.00%).

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 111 spectrofluorometer. Low-temperature (77 K) spectra were recorded by using an optical Dewar sample holder. Proton NMR spectra were recorded on a JEOL JNM-GSX270 Fourier-transform spectrometer with chemical shifts reported relative to $SiMe_4$. Emission lifetime measurements were performed using a conventional laser system. The excitation source was the 355 nm output (third harmonic) of a Quanta-Ray Q-switched GCR-150 pulsed Nd-YAG laser (10 Hz). Luminescence decay signals were recorded on a Tektronix model TDS 620A digital oscilloscope, and analysed using a program for exponential fits. All solutions for photophysical studies were prepared under vacuum in a round-bottom flask (10 cm^3) equipped with a sidearm 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.

Crystallography

Crystals of complex **3** were obtained by recrystallization from dichloromethane–hexane.

Crystal data. $C_{116}H_{104}Cu_4P_4$, M_r = 1876.18, orthorhombic, space group $Pna2_1$ (no. 33), a = 22.119(4), b = 20.796(4), c = 21.736(4) Å, U = 9998(2) Å^3, Z = 4, D_c = 1.246 g cm^{-3}, μ(Mo-Kα) = 9.51 cm^{-1}, F(000) = 3904, 298 K.

A crystal of dimensions 0.25 × 0.20 × 0.25 mm was used for data collection on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) using ω–2θ scans with ω-scan angles (0.73 + 0.35 tan θ)° at scan speeds of 16.0° min^{-1} (up to four scans). A total of 9603 reflections was collected. The intensities of three representative reflections, measured after every 300, show a decay of 7.50%. Intensity data (up to $2\theta_{max}$ = 50° in the ranges h 0–26, k 0–26, l 0–25) were corrected for decay, Lorentz and polarization effects and empirical absorption corrections were made based on azimuthal scans of four reflections (minimum and maximum transmission factors 0.958 and 1.000). 4969 Reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was determined from systematic absences and confirmed by the successful structure refinement. The structure was solved by DIRDIF 92 and PATTY and expanded using Fourier techniques[10] and refined by full-matrix least squares using TEXSAN[11] on a Silicon Graphics Indy computer. The four Cu, four P and six acetylenic C atoms were refined anisotropically and the remaining 110 phenyl and methyl C atoms isotropically. The 104 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atom were not refined. Convergence for 566 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.020F_o^2)^2]$ for 4969 reflections with $I > 3\sigma(I)$ was reached at R = 0.059 and R' = 0.064 with a goodness of fit of 2.20; $(\Delta/\sigma)_{max}$ = 0.04. The final Fourier-difference map was featureless, with maximum positive and negative peaks of 0.40 and 0.36 e Å^{-3}, respectively. Refinement of the enantiomer gave a higher R factor at 0.061.

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 186/28.

Results and Discussion

The complex $[Cu_4(PPh_3)_4(C\equiv CPh)_4]$ **1** was prepared by the reaction of $[Cu(MeCN)_4]PF_6$, phenylacetylene and an excess of triphenylphosphine and KOH in dichloromethane–methanol under anaerobic and anhydrous conditions. Attempts to prepare **2**–**4** using a similar method were unsuccessful. Instead, they were obtained by the depolymerization of $[\{Cu(C\equiv CPh)\}_n]$ with the respective tertiary phosphines. The yields were, however, rather low, probably owing to the incomplete reaction with the phosphine ligands. All the newly synthesized copper(I)

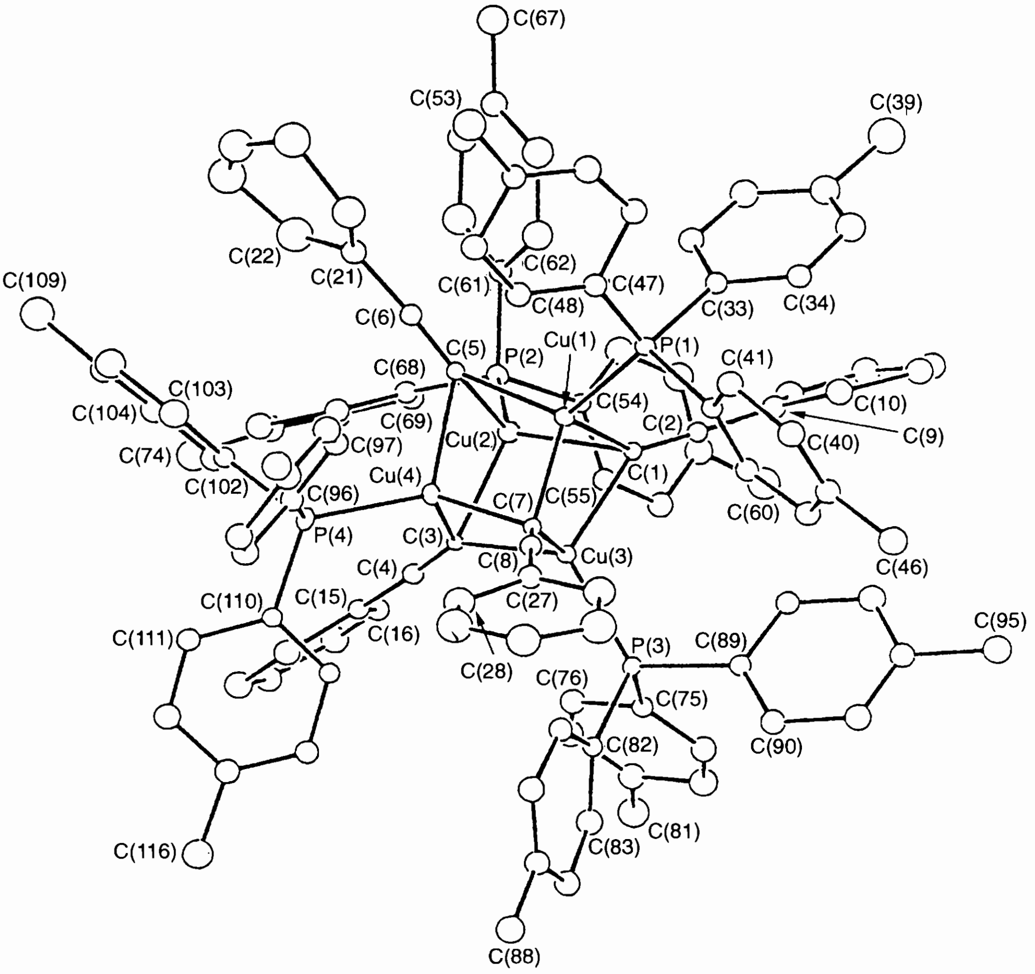


Fig. 1 Perspective drawing of $[Cu_4\{P(C_6H_4Me\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C\equiv CPh)_4]$ with atomic numbering

complexes gave satisfactory elemental analysis, and have been characterized by IR and NMR spectroscopy. The IR spectra show a medium, sharp peak at *ca.* 2020 cm^{-1}, assigned to the ν(C≡C) stretch.

Fig. 1 shows the perspective drawing of $[Cu_4\{P(C_6H_4Me\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$ **3**. The structure determination shows that the tetranuclear complex consists of an essentially tetrahedral metal skeleton bearing four terminally bonded phosphine molecules and four μ_3-η^1-phenylacetylide ligands, a distorted cubane structure similar to those observed in other tetranuclear copper(I) clusters such as $[Cu_4X_4L_4]$ (X = halide; L = N, P or As donors).[12]

The bridging modes of the acetylides are markedly asymmetric, with Cu–C contacts in the range 2.086(4)–2.237(4) Å in **1**,[9,13] 2.11(1)–2.27(1) Å in **2**[14] and 2.11(2)–2.25(2) Å in **3** (Table 1). The observed C≡C distance [1.202(6) and 1.207(6) Å for **1**;[9,13] 1.17(1) and 1.21(1) Å for **2**;[14] 1.18(2) and 1.19(2) Å for **3**] and the linearity of the phenylacetylide groups [178.0(5) and 179.2(5)° for **1**;[9,13] 177(1) and 179(1)° for **2**;[14] 176(1) and 179(1)° for **3**] are indicative of a typical C≡C bond and the absence of π back donation from the metals to the ligand π* orbitals. All the cubane complexes are 56-electron systems and hence are electron deficient.

The Cu ··· Cu distances for **1**,[9,13] **2**[14] and **3** are in the ranges 2.5092(5)–2.6635(8), 2.550(2)–2.648(2) and 2.567(2)–2.607(2) Å, respectively, indicating that the Cu_4 tetrahedrons are irregularly distorted. This may be due to intramolecular steric overcrowding between $PhC{\equiv}C^-$ and the phosphines. These distances are much shorter than that of the analogous cubane-type $[\{Cu(PPh_3)Cl\}_4]$ [3.118(1)–3.430(2) Å],[12d] $[\{Cu(PPh_3)Br\}_4]$ [3.087(2)–3.541(2) Å][12b] and $[\{Cu(PPh_3)I\}_4]$ [2.874(5)–3.164(4) Å].[12b] They are similar to that observed in metallic copper, indicating that there may be some metal–metal interaction. The shorter distances in **1**–**3** than those of the halide clusters can be explained by the greater intramolecular steric hindrance of the $PhC{\equiv}C^-/PPh_3$ than X^-/PPh_3 in the cubane structure. To minimize the non-bonding repulsion between the bulky phenyl groups, the acetylides move outward which, in order to maintain reasonable metal–acetylide bond lengths, causes the metal atoms to move inward toward the centroid of the cubane-like core. Similar observations have also been made for $[\{Cu(PEt_3)X\}_4]$[12f] and $[\{Ag(PPh_3)X\}_4]$.[15] Although no X-ray data are available for **4**, it is not unreasonable to expect that its solid-state structure is similar to that of **1**–**3**. This has been confirmed spectroscopically (see below).

The room-temperature electronic absorption spectra of complexes **1**–**4** are characterized by a high-energy absorption band at *ca.* 260 nm and a shoulder at *ca.* 320 nm with a long tail extending to 500 nm. For **1**, two additional peaks are observed at 386 and 445 nm. The bands at *ca.* 260 nm for **1**–**4** are at the same position as the absorption maxima of their corresponding free phosphines, and are assigned as intraligand transitions. The only absorption spectral feature unique to these clusters is that at long-wavelength which tails to 500 nm.

Table 1 Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[Cu_4\{P(C_6H_4Me\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$

Cu(1) ··· Cu(2)	2.580(2)	Cu(1) ··· Cu(3)	2.605(2)
Cu(1) ··· Cu(4)	2.577(2)	Cu(2) ··· Cu(3)	2.607(2)
Cu(2) ··· Cu(4)	2.595(2)	Cu(3) ··· Cu(4)	2.567(2)
Cu(1)–P(1)	2.256(4)	Cu(2)–P(2)	2.242(4)
Cu(3)–P(3)	2.235(4)	Cu(4)–P(4)	2.219(4)
Cu(1)–C(1)	2.25(1)	Cu(1)–C(5)	2.15(1)
Cu(1)–C(7)	2.11(2)	Cu(2)–C(1)	2.20(1)
Cu(2)–C(3)	2.14(2)	Cu(2)–C(5)	2.17(2)
Cu(3)–C(1)	2.17(1)	Cu(3)–C(3)	2.21(1)
Cu(3)–C(7)	2.19(1)	Cu(4)–C(3)	2.12(1)
Cu(4)–C(5)	2.25(2)	Cu(4)–C(7)	2.14(1)
C(1)–C(2)	1.19(2)	C(3)–C(4)	1.18(2)
C(5)–C(6)	1.19(2)	C(7)–C(8)	1.19(2)
Cu(1)–C(1)–C(2)	129(1)	Cu(2)–C(1)–C(2)	135(1)
Cu(3)–C(1)–C(2)	145(1)	Cu(2)–C(3)–C(4)	128(1)
Cu(3)–C(3)–C(4)	143(1)	Cu(4)–C(3)–C(4)	136(1)
Cu(1)–C(5)–C(6)	143(1)	Cu(2)–C(5)–C(6)	138(1)
Cu(4)–C(5)–C(6)	127(1)	Cu(1)–C(7)–C(8)	132(1)
Cu(3)–C(7)–C(8)	144(1)	Cu(4)–C(7)–C(8)	129(1)
C(1)–C(2)–C(9)	176(1)	C(5)–C(6)–C(21)	179(1)
C(3)–C(4)–C(15)	178(1)	C(7)–C(8)–C(27)	176(1)

Table 2 Photophysical data

Compound	Medium (*T*/K)	λ_{em}/nm (τ_o/μs)
$[Cu_4(PPh_3)_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$	Solid (298)	483 (sh) (3.7 ± 0.3) 522 (3.7 ± 0.3)
	Solid (77)	477, 524
	CH_2Cl_2 (298)*	420, 520 (sh) (< 0.01) 616 (3.6 ± 0.3)
$[Cu_4\{P(C_6H_4F\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$	Solid (298)	516 (1.3 ± 0.1)
	Solid (77)	516
	CH_2Cl_2 (298)*	420, 510 (sh) 606 (0.86 ± 0.09)
$[Cu_4\{P(C_6H_4Me\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$	Solid (298)	548 (0.52 ± 0.05)
	Solid (77)	535
	CH_2Cl_2 (298)*	410, 510 (sh), 620
$[Cu_4\{P(C_6H_4OMe\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}C{\equiv}CPh)_4]$	Solid (298)	529 (2.9 ± 0.3)
	Solid (77)	521
	CH_2Cl_2 (298)*	410, 670

* $[Cu_4] \cong 0.02$ mmol dm^{-3}.

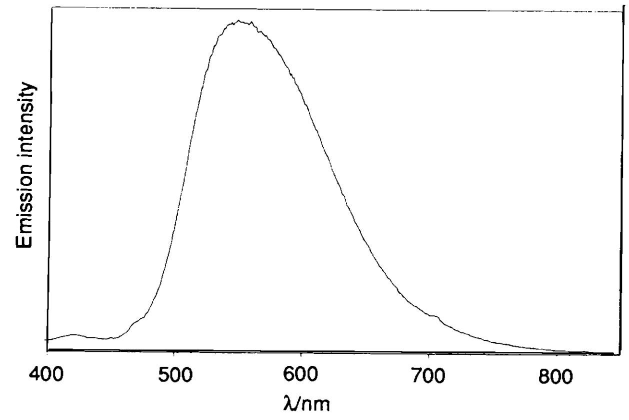


Fig. 2 Emission spectrum of $[\mathrm{Cu_4\{P(C_6H_4Me}\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}\mathrm{C{\equiv}CPh})_4]$ in the solid state at 298 K

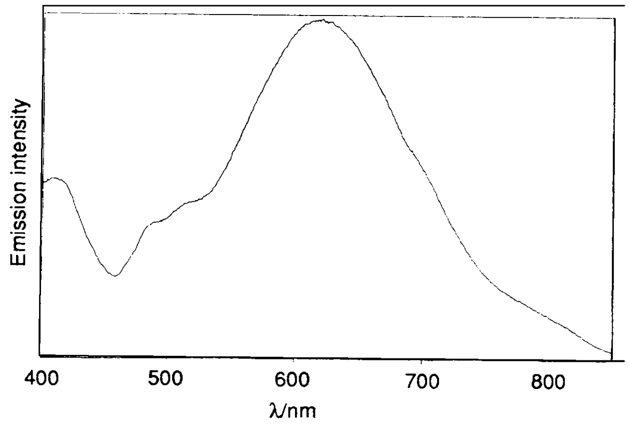


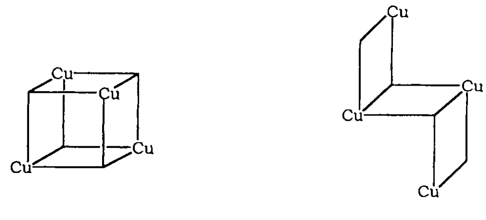
Fig. 3 Emission spectrum of $[\mathrm{Cu_4\{P(C_6H_4Me}\text{-}p)_3\}_4(\mu_3\text{-}\eta^1\text{-}\mathrm{C{\equiv}CPh})_4]$ in degassed dichloromethane at 298 K

Excitations of solid or fluid solutions of complexes **1**–**4** at $\lambda > 350$ nm produce long-lived, intense luminescence. The photophysical data are summarized in Table 2. The room-temperature and 77 K solid-state emission spectra of **2**–**4** are very similar. The solid-state emission spectrum of **3** at room temperature is shown in Fig. 2. All exhibit only an intense, unstructured, broad and asymmetric emission band in the visible region. At room temperature the emissions are centred between 516 and 548 nm and remain relatively unchanged on cooling to 77 K with the maxima only slightly blue-shifted (λ_{em}^{max} 516–535 nm). The room-temperature solid-state emission spectrum of **1** consists of a band at 522 nm with a shoulder at *ca.* 483 nm. Upon cooling to 77 K the band at 483 nm became more prominent and slightly blue-shifted to 477 nm. The long lifetimes of the luminescence (in the microsecond range at room temperature) suggest that the emissions possibly originate from spin-forbidden transitions.

The emission spectra of complexes **1**–**4** in dichloromethane at room temperature are again very similar. That of **3** is presented in Fig. 3. All spectra consist of two bands centred at *ca.* 420 and 620 nm. In addition, a shoulder at *ca.* 520 nm appeared on the high-energy side of the band at 620 nm.

In view of the short Cu ··· Cu distances observed in complexes **1**–**3** it is likely that the emissive states are derived from metal-centred excited states modified by metal–metal interactions. The metal–metal interaction arises from configurational mixing of the filled d orbitals with the empty orbitals derived from higher-energy 4s and 4p atomic orbitals of the $\mathrm{Cu_4}$ units. Emissions from d ⟶ s excited states of similar energies ($\lambda_{em} \approx 540$ nm) are also observed in other copper(I) systems.[16] On the other hand, the excited state can also be assigned as a $\mathrm{PhC{\equiv}C{\rightarrow}Cu_4}$ acetylide-to-metal charge-transfer transition (l.m.c.t.) owing to the good σ-donating property of the phenylacetylide ligands. An l.m.c.t. $\mathrm{X^-{\rightarrow}Cu_4}$ excited state has also been suggested by Ford and co-workers[2a–e] to account for the luminescence properties of the $[\mathrm{Cu_4I_4(py)_4}]$ cubane cluster, which bears structural resemblance to the present system. Therefore, we favour the assignment of the emission to spin-forbidden transitions derived from triplet excited states of d ⟶ s/l.m.c.t. admixture. Similar assignments have been made for the related trimeric copper(I)–phenylacetylide–phosphine systems.[1c]

Although no X-ray data are available for complex **4**, it is reasonable to expect that its solid-state structure is similar to that of **1**–**3** in view of the similarity of its excitation and emission spectra to those of **1**–**3**. The possibility that **4** is a chair species in the solid state, which has the same empirical formula as a cube, has been eliminated on spectroscopic grounds. The transition between the lowest unoccupied (LUMO) and highest occupied (HOMO) molecular orbitals is at lower energy for the cube isomer because the delocalization over the 3d and 4s orbitals of the copper atoms is larger than that in the chair. This is rationalized by the fact that in the cube isomer each of the four copper atoms has three neighbouring copper atoms while in the chair isomer only two of the coppers have three neighbouring copper atoms and the other two have only two. Thus the chair isomer should emit at higher energies than the cube. A comparison of the luminescence between the two isomers of tetrameric silver(I) clusters has been discussed by Henary and Zink.[5] Owing to the structural and spectroscopic similarities, the emissions of **4** are also assigned as derived from d ⟶ s/l.m.c.t. admixture.



Cube isomer

Chair isomer

It is interesting that whether the origin of the excited state is d ⟶ s, l.m.c.t. or d ⟶ s/l.m.c.t. admixture, the lowest-energy transition would involve the promotion of an electron to an empty bonding s orbital, that is the LUMO would remain σ bonding with regard to the metal cluster core, resulting in an excited state that is strongly contracted and distorted owing to an increase in Cu ··· Cu bonding in the excited state.[17] Such a distortion would be one of the factors accounting for the large Stokes shift observed for the above copper(I) complexes. The red shift of the low-energy luminescence in solution may also be ascribed to rigidochromic effects where larger structural changes can take place in solution but not in the rigid lattice of the solid. Similar red shifts have been reported for the $[\mathrm{Cu_4I_4L_4}]$ clusters.[18]

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