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Luminescent high nuclearity Cu(I)-alkynyl clusters, $[Cu_{16}(hfac)_8(3,3\text{-dimethyl-1-butynyl})_8]$ and $[Cu_{20}(hfac)_8(3\text{-phenyl-1-propynyl})_{12}]$

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Two novel high nuclearity copper(I) alkynyl complexes, $[Cu_{16}(hfac)_8(C\equiv CBu^t)_8]$ (**1**) and $[Cu_{20}(hfac)_8(C\equiv CCH_2Ph)_{12}]$ (**2**), that consist of complicated alkynyl bridged Cu(I) cores 'capped' by peripheral hfac ligands have been synthesised and characterised by X-ray structure determination. The photoluminescent properties of **1** and **2** together with the clusters, $[Cu_{18}(hfac)_{10}(C\equiv CBu^n)_8]$ (**4**) and $[Cu_{26}(hfac)_{11}(C\equiv CPr^n)_{15}]$ (**5**) and the monomeric species, $[Cu(hfac)(HC\equiv CCH_2OMe)]$ (**3**), $[Cu(hfac)(Me_3SiC\equiv CSiMe_3)]$ (**6**) and [Cu(hfac)(COD)] (**7**) are reported. A comparison of the photoluminescent spectra of the high nuclearity species with the related monomeric complexes have shown that the cluster luminescence is derived from transitions within the delocalised Cu-hfac chelate ring.

Introduction

Transition metal-alkynyl chemistry has attracted much attention,[1–3] partly because the alkynyl ligands provide a variety of metal bridging modes allowing polynuclear complexes with a wide range of structures to be generated. The high degree of electron delocalisation, the presence of polarizable moieties and the presence of metal–metal interactions mean that these systems have potential applications in non-linear optics,[4,5] luminescence[2,4,6–19] and molecular conductivity.[20]

Discrete mono- and poly-nuclear Cu(I)-alkynyl species have been synthesised[21–32] but the propensity for the alkynyl ligand to multiply bridge Cu(I) atoms makes the generation of discrete high nuclearity complexes difficult due to the uncontrollable formation of polymeric materials. Recent work in our laboratory has shown that discrete Cu(I)-alkynyl clusters with the general formula, $[Cu_{x+y}(hfac)_x(alkynyl)_y]$, where $hfac^-$ is 1,1,1,5,5,5-hexafluoropentanedionate, can be easily isolated from the reaction of Cu_2O with hfacH in the presence of an excess of a terminal alkyne.[33,34] X-Ray structure determinations of $[Cu_{18}(hfac)_{10}(C\equiv CBu^n)_8]$ and $[Cu_{26}(hfac)_{11}(C\equiv CPr^n)_{15}]$ have been reported.[33,34] The stability of these polynuclear alkynyl copper(I) complexes appears to depend on the presence of the hfac ligands which effectively 'cap off' the edges of the clusters, preventing formation of polymeric systems, and the size of the clusters increases with the alkyne : hfac ratio in the complex.

The documentation of photoluminescent behaviour of copper(I) alkyne complexes has generated considerable interest[2] and we have shown that this extends to the cluster $[Cu_{18}(hfac)_{10}(hexynyl)_8]$.[34] In this paper we extend the studies of photoluminescent behaviour of copper(I) compounds, making comparisons between clusters of the type $[Cu_{x+y}(hfac)_x(alkynyl)_y]$ and related mononuclear complexes. Two new clusters, $[Cu_{16}(hfac)_8(C\equiv CBu^t)_8]$ (**1**) and $[Cu_{20}(hfac)_8(C\equiv CCH_2Ph)_{12}]$ (**2**) have been characterised and their structures are compared to others that have been determined recently.

Experimental

Instrumentation

^1H NMR spectra were obtained on Bruker AC 200 and AC 250 instruments. UV-Vis absorption spectra on an ATI UNICAM UV/vis spectrometer with 1 cm path length quartz cuvettes, FTIR spectra on a Perkin-Elmer Paragon 1000 spectrometer as KBr discs and fluorescence spectra on a Yobin-Yvon Fluoro-Max Photon Counting Spectrometer.

Materials and reagents

[Cu(hfac)(COD)] (COD = cyclooctadiene) was prepared using a reported method.[35] $[Cu(hfac)(Me_3SiC\equiv CSiMe_3)]$ and all other reagents were obtained from Aldrich chemicals and used without further purification. *n*-Hexane was distilled from sodium–benzophenone–tetraglyme (trace) under N_2. N_2 gas was dried with 4 Å molecular sieves and deoxygenated with BTS catalyst.[36] All preparations of copper(I) complexes were carried out under anaerobic and anhydrous conditions using standard Schlenk techniques. 3,3-Dimethyl-1-butyne, 3-phenyl-1-propyne and 1,1,1,5,5,5-hexafluoropentan-2,4-dione (hfacH) were degassed by freeze/vac/thaw cycles.

Syntheses

$[Cu_{16}(hfac)_8(C\equiv CBu^t)_8]$ (1). Cu_2O (1.64 g, 11.5 mmol) and anhydrous $MgSO_4$ (*ca.* 2 g) were added to a solution of 3,3-dimethyl-1-butyne (5 g, 0.061 mol) in hexane (10 ml). Dropwise addition of hfacH (2.5 ml, 18 mmol) was accompanied by an exothermic reaction. After stirring for 18 h at room temperature the mixture was cannula-filtered and the solid residue washed with hexane (3 × 10 ml). The combined lime green filtrate and washings were evacuated *in vacuo* and the resulting orange/yellow oil was heated *in vacuo* at 65 °C for 2 h and then dissolved in refluxing hexane (20 ml) and set aside at 4 °C. After 48 h dark red crystals suitable for X-ray diffraction studies had separated. The supernatent liquid was removed and the crystals were washed with hexane and dried *in vacuo*. Yield: 0.446 g (12%). Found: C, 33.39; H, 2.71. Calc. for $C_{88}H_{80}O_{16}Cu_{16}F_{48}\cdot C_6C_{14}$: C, 33.12; H, 2.78%. δ_H (CD_2Cl_2, 250 MHz): 1.41 (s, 72 H, CH_3) and 6.03 (s, 8 H, CH). δ_F (CD_2Cl_2, 250 MHz): −76.73 (s, 48 F, CF_3). IR spectra (KBr disc): 2937s, 2874m, 2405w, 1860m, 1638s, 1555s and 1466s cm^{-1}.

$[Cu_{20}(hfac)_8(C\equiv CCH_2Ph)_{12}]$ (2). Cu_2O (1.64 g, 11.5 mmol) and anhydrous $MgSO_4$ (*ca.* 2 g) were added to a cooled (0 °C) solution of hfacH (2.5 ml, 18 mmol) and 3-phenyl-1-propynyl

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Table 1 Crystallographic data for complexes **1**, **2** and **3**

	1	**2**	**3**
Empirical formula	$C_{88}H_{80}Cu_{16}F_{48}O_{16}$	$C_{148}H_{92}Cu_{20}F_{48}O_{16}$	$C_9H_7CuF_6O_3$
Formula weight	3322.16	4309.02	340.69
Temperature/K	150(2)	150(2)	260(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system	Tetragonal	Monoclinic	Monoclinic
Space group	*P*-4*n*2	*P*2$_1$/*c*	*P*2$_1$/*n*
a/Å	16.7029(10)	27.149(4)	16.276(9)
b/Å	16.7029(10)	22.902(4)	4.635(3)
c/Å	21.9360(19)	27.428(4)	16.522(9)
β/°		115.969(2)	99.627(9)
Volume/Å^3	6119.9(7)	15332(4)	1228.9(11)
Z	2	4	4
Absorption coefficient/mm^{-1}	2.841	2.827	1.853
F(000)	3264	8480	672
Crystal size/mm^3	0.45 × 0.45 × 0.45 (orange block)	0.80 × 0.40 × 0.40	0.83 × 0.22 × 0.19
Reflections collected	33913	76769	6898
Independent reflections	6274 [*R*(int) = 0.0389]	27227 [*R*(int) = 0.0437]	2872 [*R*(int) = 0.0301]
Absorption correction	SADABS[38]	SADABS[38]	SADABS[38]
H-atom placement	Geometric	Geometric	Geometric
Data/restraints/parameters	6274/60/419	27227/3708/2163	2872/25/204
R_1 [$\|F\| > 4\sigma(\|F\|)$]	0.0360	0.0412	0.04670
wR_2 [All data]	0.0718	0.1124	0.1059

(5 g, 43 mmol) in hexane (10 ml). After stirring for 48 h at room temperature the mixture was treated in the manner described above. Orange crystals suitable for X-ray structure determination separated from the hexane solution after 24 h. Yield: 1.09 g (14%). Found: C, 41.34; H, 2.07. Calc. for $Cu_{20}C_{148}H_{92}O_{16}F_{48}$: C, 41.25; H, 2.15%. δ_H (CD_2Cl_2, 250 MHz): 3.55–3.68 (m, 24 H, CH_2), 5.95 (s, 8 H, C*H*) and 7.12–7.16 (m, 60 H, Ar*H*). δ_F (CD_2Cl_2, 250 MHz): −76.67 (s, 48 F, CF_3). IR spectra (KBr disc): 3064m, 3029m, 2360w, 1945w, 1637s, 1553s and 1467s cm^{-1}.

[Cu(hfac)(HC≡CCH$_2$OMe)] (3). Cu_2O (1.64 g, 11.5 mmol) and anhydrous $MgSO_4$ (*ca.* 2 g) were added under N_2 to methyl 2-propynyl ether (5 g, 71 mmol). hfacH (2.5 ml, 18 mmol) was added dropwise, followed by hexane (10 ml). After stirring for 4 h the mixture was cannula filtered and yellow crystals separated over several days from the green/yellow filtrate. Yield: 1.09 g (14%). Found: C, 31.63; H, 1.96. Calc. for $CuC_9H_7O_3F_6$: C, 31.73; H, 2.07%. IR spectra (KBr disc): 1672s, 1654s, 1314w, 1256s, 1208s, 1148s, 789m, 768w, 736w, 662s, 579m and 525w cm^{-1}.

Crystallography

All data sets were collected with MoKα radiation on a Bruker Smart APEX CCD diffractometer equipped with an Oxford Cryosystems low-temperature device. The data collection temperature was 150 K for the two polynuclear complexes, but this caused severe degradation in the quality of crystals of [Cu(hfac)(HC≡CH$_2$OMe)], and the data set for this compound was collected at 260 K. Absorption corrections were performed with the program SADABS, and the structures were solved by direct methods (SHELXTL).[37] Refinement was carried out against F^2 using all data (SHELXTL) with H-atoms in calculated positions and anisotropic displacement parameters (adps) for all non-H atoms. All the structures suffered from high librational motion in the CF_3 groups. Rotational disorder was modelled for groups for which the maximum eigenvalue of the U_{ij} tensor was more than 0.3 at full occupancy. In these cases both components were restrained to be geometrically similar and to have local three-fold symmetry, and their relative occupancies were refined. 'Opposite' F-atoms were either constrained or restrained to have equal adps. In the structure of [Cu$_{16}$(hfac)$_8$(C≡CBu^t)$_8$] the molecule resides on a 2.22 special position in this structure (Wyckoff position 2d). One Bu^t group is disordered over two orientations, and this was treated in the same fashion as the disordered CF_3 groups. A disordered solvent region was treated in the manner described by van der Sluis and Spek,[39] further details of this procedure are given in the deposited CIF. In the structure of [Cu$_{20}$(hfac)$_8$(C≡CCH$_2$-Ph)$_{12}$] one phenyl group is positionally disordered over two sites. The relative occupancies were refined; the positional parameters were subject to similarity restraints applied to the geometries of the part-weight fragments and rigid bond and body restraints were applied to the adps. Crystal data and refinement details are summarised in Table 1.

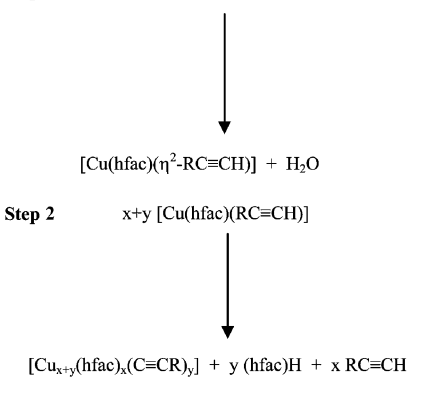
CCDC reference numbers 190272–190274.

See http://www.rsc.org/suppdata/dt/b2/b207106c/ for crystallographic data in CIF or other electronic format.

Results and discussion

The facile preparations of the new Cu$_{16}$ and Cu$_{20}$ clusters **1** and **2** involve conditions similar to those described for [Cu$_{18}$(hfac)$_{10}$(C≡CBu^n)$_8$] (**4**) and [Cu$_{26}$(hfac)$_{11}$(C≡CPr^n)$_{15}$] (**5**).[33,34] The isolation of clusters with very different nuclearities and structures when the only difference in the preparation involves the nature of the alkyne is a feature of considerable interest. The assembly of the alkynyl-bridged complexes takes place on heating *in vacuo* when both hfacH and 1-alkyne are removed from the system. Their recovery has been confirmed by condensation in traps and analysis. These observations are consistent with the two steps outlined in Scheme 1.

Under these circumstances the relative volatilites and pK_as of the alkyne and hfacH are likely to be important in determining the outcome of the reaction. So too is the bulk of the alkyne



Scheme 1 Proposed cluster formation mechanism.

substituent. The clusters have a very anisotropic distribution of the hfac$^-$ and alkynyl$^-$ ligands (*vide infra*), with alkynyl ligands being located in the centre of the cluster and the Cu(I)-hfac units on the periphery, in a "capping mode". As a consequence the larger clusters have a higher alkynyl : hfac ratio and their formation will be favoured by preferential removal of hfacH from the system during the condensation process.

Once formed from the condensation process, and once the hfac : alkynyl ratios in the system have been fixed, there is no evidence for **1** and **2** undergoing any rearrangement in non-coordinating solvents such as hexane or dichloromethane, and both **1** and **2** were recrystallised from hexane to generate compounds that have been characterised by X-ray crystallography, IR, ^{1}H NMR, ^{19}F NMR and elemental analysis.

The ^{1}H NMR spectrum of **1** shows peaks corresponding to the *tert*-butyl protons and the hfac$^-$ proton at 1.41 and 6.03 ppm respectively with intensities in the expected ratio for the 8 : 8 stoichiometry of the ligands in the cluster. The sharpness of these signals and the singlet for all the CF_3 groups in the ^{19}F NMR spectrum (−76.73 ppm) implies that the clusters are fluxional and/or that ligand exchange is rapid. The ^{1}H NMR of **2** contains multiplets at 7.12–7.16 and 3.55–3.68 ppm corresponding to the phenyl rings and the methylene groups of the 3-phenyl-1-propynyl ligand and a singlet at 5.96 ppm for the hfac proton. The ^{19}F NMR shows a sharp singlet for all the CF_3 groups at a very similar shift, −76.67 ppm, to that in **1**.

The mononuclear complex, $[(hfac)Cu(HC\equiv CCH_2OMe)]$ (**3**), was prepared to allow comparisons to be made with the polynuclear alkynyl complexes. The preparation was carried out under conditions similar to those for the first stage of the cluster preparation using anhydrous/degassed hexane as solvent.

Yellow crystals suitable for X-ray structure determination separated directly from the reaction solution. The complex (Fig. 1) has a trigonal planar disposition of the hfac oxygen atoms and the alkyne bond, with deviations from the least squares plane defined by the donor atoms of 0.0329, 0.0072, −0.0073, −0.0173 and 0.0174 Å for Cu(1), O(1), O(2), C(6) and C(7) respectively. The symmetrical coordination of the alkyne atoms C(6) and C(7) and the large deviation of the C(6)–C(7)–C(8) angle, 163.1(3)°, from linearity is consistent with a strong metal to ligand π* bonding interaction.

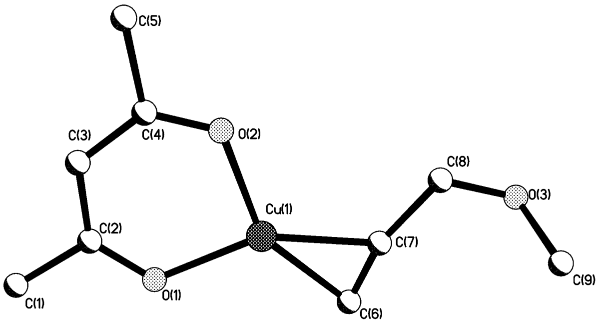


Fig. 1 The structure of $[Cu(hfac)(HC\equiv CCH_2OMe)]$ (**3**). Bond lengths from Cu(1) to O(1) and O(2) are 1.957(2) and 1.953(2) and to C(6) and C(7) are 1.944(3) and 1.961(3) Å respectively. Angles (°) defined at the copper atom by pairs of donor atoms are: O(1)–O(2), 94.61(9); O(2)–C(7), 113.62(11); C(7)–C(6) 36.02(12); C(6)–O(1), 115.69(11); O(1)–C(7), 151.71(10); O(2)–C(6), 149.54(11).

The terminal hydrogen atom attached to C(6) was located on a difference Fourier map and refined satisfactorily (C(6)–H(6A) = 0.91(2) Å) confirming that a neutral form of the ligand is present.

The solid state structure of $[Cu_{16}(hfac)_8(C\equiv CBu^t)_8]$ is shown in Fig. 2. The cluster is composed of four crystallographically independent copper atoms, Cu(1)–Cu(4), two hfac and two 3,3-dimethyl-1-butynyl ligands. The remainder is generated by two mutually perpendicular C_2 axes. The Cu(I) atoms are located in two shells. Eight, Cu(1, 1A, 1B, 1C 4, 4A, 4B and 4C), in the inner shell form a tightly packed cage, bridged exclusively by alkynyl ligands. The eight atoms, Cu(2, 2A, 2B, 2C, 3, 3A, 3B and 3C), in the outer shell are bonded to hfac ligands and each of these Cu(I)-hfac capping units is then linked to the inner shell by an η^2-interaction with a *tert*-butylacetylenyl ligand. The hfac and alkynyl ligands are distributed unevenly over the cluster with the hfac units forming a girdle around the widest part of the cluster and the alkynyl units located inside this girdle, lying approximately perpendicular to the plane it defines (Fig. 2).

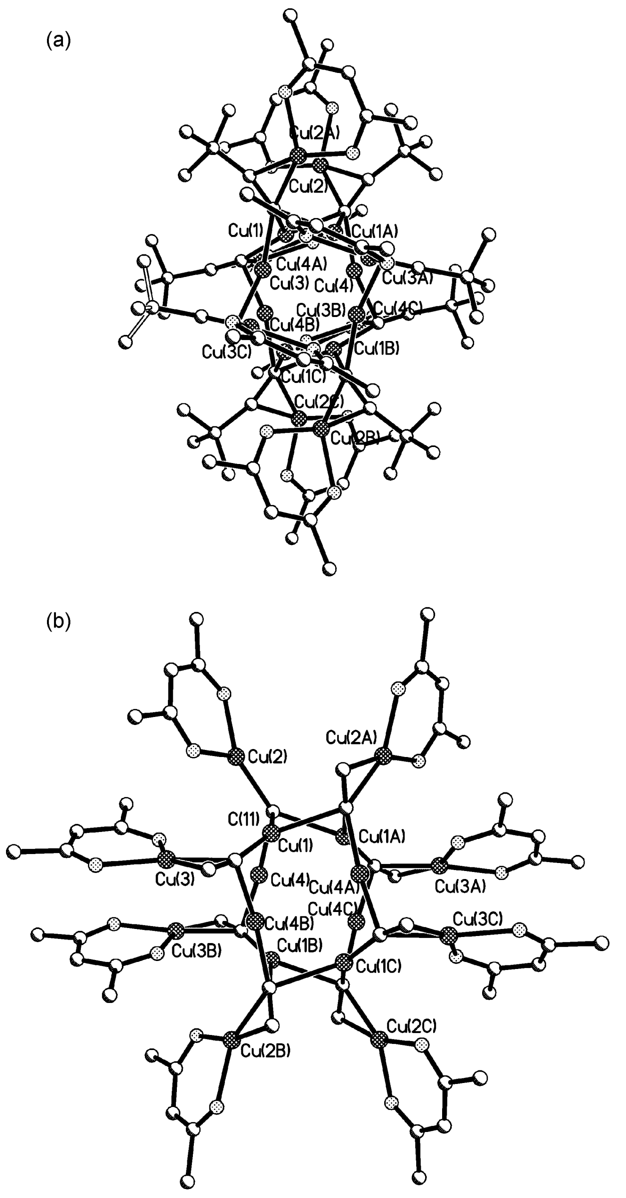


Fig. 2 $[Cu_{16}(hfac)_8(C\equiv CBu^t)_8]$ (**1**). For clarity no F and H atoms or Cu ··· Cu interactions are shown. In (a) only one of the disordered sites of each of the Bu^t groups is displayed. In (b) all of the *tert*-butyl groups of the alkynyls are removed.

The linkages defining the networks of the clusters described in this paper are shown in Fig. 3. In $[Cu_{16}(hfac)_8(C\equiv CBu^t)_8]$ the outer shell copper atoms are all present as the Cu(hfac) part of the type **A** linkages and the inner shell copper atoms Cu(1) and Cu(4) and their symmetry-related partners are the bridging atoms in the linkages **B** and **C**.

In $[Cu_{16}(hfac)_8(C\equiv CBu^t)_8]$ the two crystallographically independent **A** linkages contain alkyne bonds, C(17)–C(18) and C(11)–C(12) with lengths, 1.253(5) and 1.265(5) Å respectively, very similar to those found in the clusters reported previously.[33,34] They are slightly longer than the C–C distances found

Table 2 Selected contact and bond distances (Å) and angles (°) in **1**

Cu ··· Cu distances in the inner shell			
Cu(1) ··· Cu(4)	2.5159(6)	Cu(1) ··· Cu(1A)	2.6116(8)
Cu(1) ··· Cu(4A)	2.8548(6)	Cu(1) ··· Cu(4B)	2.6428(6)
Cu(1A) ··· Cu(4)	2.8548(8)		
Cu ··· Cu distances between inner and outer shell atoms			
Cu(1) ··· Cu(2)	2.7595(7)	Cu(1) ··· Cu(2A)	3.954(1)
Cu(1) ··· Cu(3)	3.1698(7)	Cu(4) ··· Cu(3B)	3.0430(7)
Cu(4) ··· Cu(2)	3.667(1)		
Alkynyl bond lengths			
C(11)–C(12)	1.265(5)	C(17)–C(18)	1.253(5)
Bond angles			
C(12)–C(11)–Cu(4)	134.2(3)	C(18)–C(17)–Cu(1)	167.6(3)
C(12)–C(11)–Cu(1)	147.0(3)	C(17)–C(18)–C(19)	158.9(4)
C(11)–C(12)–C(13))	162.2(4)		

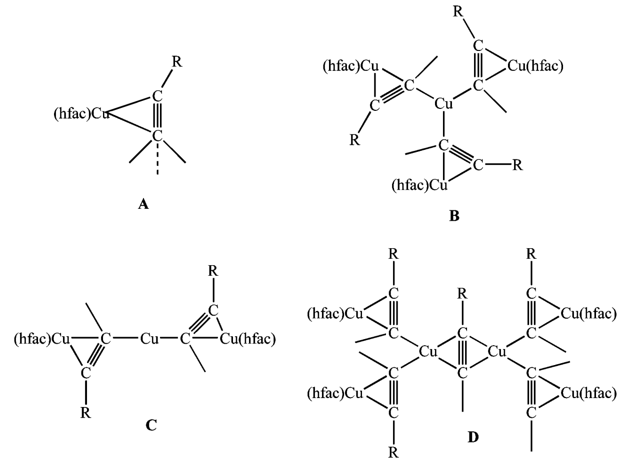


Fig. 3 The linkages, based on connectivites with Cu–C ≤ 2.505(6) Å, defining the networks in $[Cu_{16}(hfac)_8(C{\equiv}CBu^t)_8]$ and $[Cu_{20}(hfac)_8(C{\equiv}CCH_2Ph)_{12}]$. **A** is either μ_3-$(\eta_\sigma{}^1)^2(\eta_\pi{}^2)$ or μ_3-$(\eta_\sigma{}^1)^3(\eta_\pi{}^2)$.

in σ-bonded compounds[3] suggesting that the copper coordination to the alkyne π-system involved in **A** causes a bond weakening.

The bond angles between the alkynyl group and the Bu^t C-atom carbon in **A**, C(17)–C(18)–C(19) and C(11)–C(12)–C(13), are 158.9(4) and 162.2(4)° respectively. The significant distortion from linearity is consistent with a change in hybridisation resulting from the π-bonding of the (hfac)Cu to the alkynyl.[3]

The terminal alkynyl atom in **A** forms two bonds to Cu atoms with lengths in the range 1.933(3) to 2.014(3) Å. In addition there is a third longer C ··· Cu interaction, (2.270(4) Å) which must be at best only weakly bonding.

The Cu–C–C bond angles formed at the central bridging Cu atoms Cu(1) and Cu(4) in the units **B** and **C** (Fig. 3) fall into the range 134.2(3)–167.6(3)° (Table 2), suggesting that Cu–C interactions are not conventional σ bonds but include a contribution from either π or π* alkynyl orbitals.

Cu ··· Cu distances in the interior of the cluster range between 2.5159(6) and 3.0430(7) Å (Table 2). These indicate the presence of some weak metal-metal bonds as several of these contacts are shorter that twice the van der Waals radius of copper (2.8Å).[38]

The Cu_{20} cluster **2** has no crystallographically imposed symmetry. As in **1** the hfac ligands are associated with copper atoms at the extremities of the cluster, with all eight (hfac)Cu units forming π-bonds to alkynyl ligands as in the linkage **A** in Fig. 3. These alkynyl groups thus function as μ_3-$(\eta_\sigma{}^1)^2(\eta_\pi{}^2)$ or μ_4-$(\eta_\sigma{}^1)^3(\eta_\pi{}^2)$ ligands (Fig. 4).

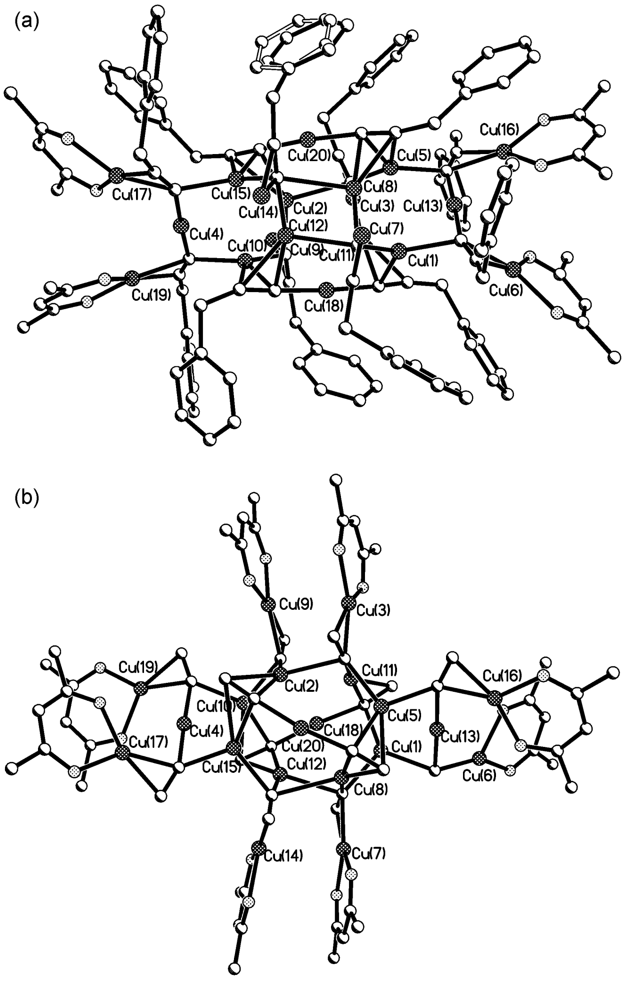


Fig. 4 Plots of $[Cu_{20}(hfac)_8(C{\equiv}CCH_2Ph)_{12}]$ (**2**). For clarity no F and H atom interactions are shown, in (a) the hfac ligands coordinated to Cu (3, 7, 9 and 14) have been removed and in (b) all the benzyl groups have been removed.

The remaining alkynyl groups hold the central core of twelve copper atoms together *via* a contribution of σ-bonds shown in the bridging units **B** and **C** in Fig. 3 and the σ and π bonds in unit **D**. The μ_3-$(\eta_\pi{}^2)_2$ alkynyl units (**D**) are not observed in the Cu_{16} cluster. These Cu_2C_2 units have a 'butterfly' configuration with Cu–$C_{terminal}$ and Cu–C_β lengths falling in the ranges 2.034(5)–2.095(5) and 2.241(6)–2.519(5) Å respectively. They define the four-coordinate geometries for the central atoms Cu(5, 8, 10, 12 and 15). These and Cu(1, 2, 11, 18 and 20) have an approximately spherical distribution, lying within 2.16 to 2.99 Å of their centroid. The alkynyl ligands are all bonded to one or more of the ten Cu atoms on this sphere. One diameter of the sphere Cu(18) ··· Cu(20), 4.93 Å defines the minimum dimension of the copper cluster. Addition of 'type **A**' units extends the cluster in two directions approximately perpendicular to this axis to create an ellipsoid with dimensions of *ca.* 8.7 Å [mean of Cu(3) ··· Cu(7), 8.758(10) and Cu(9) ··· Cu(14), 8..681(11) Å] and of *ca.* 12.7 Å [mean of Cu(6) ··· Cu(19), 12.596(11) and Cu(16) ··· Cu(17), 12.790(10) Å]. Hence, as in earlier examples, the hfac ligands can be said to operate in a capping role, defining the extremities whilst the alkynyl ligands are an integral part of the core.

Four of the central atoms Cu(4, 13, 18 and 20) are formally two coordinate as in **C**, Fig. 3, and almost linear (Table 3). One Cu atom in the core, Cu(11), is not present in any of the bonding modes shown in Fig. 3, but is instead σ-bonded to one alkynyl group and π-bonded to another.

Cu ··· Cu interatomic distances (Table 3) range between 2.4803(9) and 3.0190(9) Å. Eighteen of these separations are

Table 3 Selected bond angles (°) and bond and contact distances (Å) in **2**

Bond angles			
C(41)–Cu(4)–C(50)	177.8(3)	C(140)–Cu(20)–C(131)	171.5(2)
C(122)–Cu(18)–C(113)	173.7(2)	C(95)–Cu(13)–C(104)	178.2(3)
Cu ··· Cu contact distances			
Cu(1) ··· Cu(13)	2.5195(10)	Cu(5) ··· Cu(8)	2.8773(10)
Cu(1) ··· Cu(8)	2.6223(10)	Cu(5) ··· Cu(20)	2.9618(11)
Cu(1) ··· Cu(18)	2.7888(11)	Cu(6) ··· Cu(13)	2.9289(11)
Cu(1) ··· Cu(11)	2.8443(10)	Cu(7) ··· Cu(8)	3.0193(10)
Cu(2) ··· Cu(10)	2.6235(10)	Cu(8) ··· Cu(12)	2.6030(10)
Cu(2) ··· Cu(11)	2.7555(11)	Cu(8) ··· Cu(20)	2.7543(10)
Cu(2) ··· Cu(20)	2.7574(10)	Cu(10) ··· Cu(18)	2.9096(11)
Cu(2) ··· Cu(9)	2.8999(10)	Cu(10) ··· Cu(12)	2.9917(10)
Cu(2) ··· Cu(15)	3.0597(10)	Cu(11) ··· Cu(18)	2.7051(10)
Cu(3) ··· Cu(11)	2.8816(9)	Cu(12) ··· Cu(15)	2.5948(10)
Cu(4) ··· Cu(15)	2.4806(10)	Cu(12) ··· Cu(18)	2.8565(10)
Cu(4) ··· Cu(10)	2.4853(10)	Cu(12) ··· Cu(14)	2.8839(10)
Cu(4) ··· Cu(17)	2.7265(10)	Cu(13) ··· Cu(16)	2.7226(10)
Cu(4) ··· Cu(19)	2.7561(10)	Cu(15) ··· Cu(20)	2.7352(11)
Cu(5) ··· Cu(13)	2.5018(10)	Cu(5) ··· Cu(11)	2.5900(10)
Bond lengths in π-bonded butterfly units (**D**, Fig. 3)			
Cu(10)–C(113)	2.078(5)	Cu(15)–C(131)	2.095(5)
Cu(10)–C(114)	2.264(5)	Cu(15)–C(132)	2.519(5)
Cu(12)–C(113)	2.034(5)	Cu(5)–C(140)	2.085(5)
Cu(12)–C(114)	2.290(5)	Cu(5)–C(141)	2.346(6)
Cu(2)–C(131)	2.058(5)	Cu(8)–C(140)	2.041(5)
Cu(2)–C(132)	2.381(6)	Cu(8)–C(141)	2.241(6)

Table 4 Photophysical data (nm) for complexes **1**–**7** in *n*-hexane at RT

	Absorption (ε_{max}/dm^3 mol^{-1} cm^{-1})	Excitation λ_{em}, 400 nm	Emission λ_{ex}, 280 nm	Emission λ_{ex}, 330 and 340 nm
1	287 (104551)	292	344	366
	333sh (36285)	330, 356*		382
	453sh (2214)			
2	281 (188376)	292	344	366
	338sh (43086)	334, 357*		383
	423sh (23046)			
3	291 (14551)	289	345	368
	330 (6251)	336, 357*		383
4	281sh (99420)	293	344, 307*	367*
	305 (89480)	336, 357*, 379*		382
	437br,sh (8822)			
5	285 (259421)	294	343	366
	330 (95576)	333, 357*		380
	379 (27307)			
6	245 (17529)	293, 357*	345	368
	279.16 (16889)			
	327 (6813)	327		383
7	290 (16042)	292	343	366
	328 (6318)	331, 356*		383

* Denotes solvent Raman bands.

less than twice the van der Waals radius of Cu (2.8 Å), suggesting that, as in **1**, some weak metal–metal bonding is present in the cluster.

Fluorescence spectroscopy

The photophysical spectroscopic data for **1** and **2** are shown in Table 4 along with the data for the two clusters reported previously, [Cu$_{18}$(hfac)$_{10}$(C≡CBu^n)$_8$] (**4**)[33] and [Cu$_{26}$(hfac)$_{11}$(C≡CPr^n)$_{15}$] (**5**).[34] Data for the mononuclear complexes [Cu(hfac)(HC≡CCH$_2$OMe)] (**3**), [Cu(hfac)(Me$_3$SiC≡CSiMe$_3$)] (**6**) and [Cu(hfac)(COD)] (**7**) are included for comparison. The UV-vis spectra of **1**, **2**, **4** and **5** are very similar. The highest energy band (280–287 nm) and a shoulder at 300–330 nm can be assigned to internal ligand transitions (π ⟶ π*, n ⟶ π*). In addition, each cluster shows one weak absorption in the region 379 and 453 nm which can be tentatively assigned to M ⟶ L or L ⟶ M charge transfer within the highly delocalised Cu-alkynyl bridging networks.

All four clusters also show very similar excitation and emission spectra. The shape and relative intensities of the peaks in the overlaid excitation and emission spectra of **1** (Fig. 5) are representative of those of all the clusters. The excitation spectra ($\lambda_{emission}$, 400 nm) of **1**, **2**, **4** and **5** contain bands in the region 291–293 and 329–335 nm to which the luminescent properties can be attributed.

Emission spectra obtained are very similar for all four clusters (Table 4). For excitation at 280 nm intense emissions at *ca.* 344 nm are observed and with λ = 330 and 340 nm at *ca.* 366 and 383 nm respectively. It is unlikely that the luminescent properties of these clusters are due to MLCT, LMCT and intra-ligand charge transfer within the extensively bridged Cu-alkynyl networks because all the clusters show remarkably similar spectra despite the fact that each has a different Cu

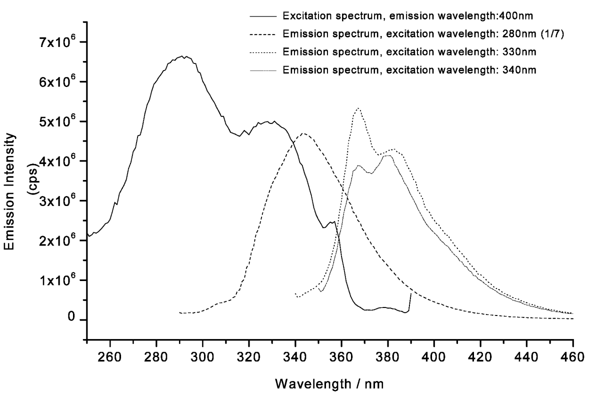


Fig. 5 Overlaid excitation and emission solution spectra of [Cu(hfac)$_8$-(C≡CBu^t)$_8$] (**1**) in *n*-hexane.

nuclearity and core structure. The possibility that the bands arise from Cu(hfac) components was considered by comparing emission spectra with those of the mononuclear complexes, [Cu(hfac)(HC≡CCH$_2$OMe)] (**3**), [Cu(hfac)(Me$_3$SiC≡CSiMe$_3$)] (**6**) and [Cu(hfac)(COD)] (**7**).

The excitation spectra for all three complexes are remarkably similar with intense bands between 289–293 nm and 330–336 nm (Table 4). Their emission spectra are also very similar (Table 4) and are typified by those shown for **3** in Fig. 6.

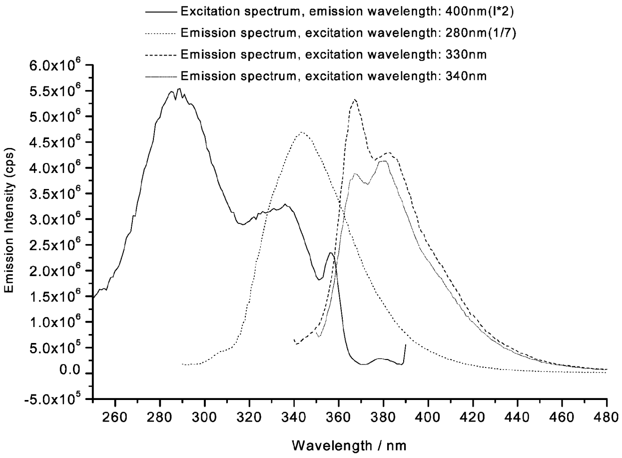


Fig. 6 Overlaid excitation and emission solution spectra of [Cu(hfac)-(HC≡CCH$_2$CCH$_2$OMe)] (**3**) in *n*-hexane.

It is clear that the clusters and related mononuclear complexes display almost identical luminescent behaviour despite the considerable differences in their structures and sizes. As the Cu(I)-hfac moiety is the only common feature within all of these molecules it appears that the luminescent properties are derived from the delocalised electronic system in this chelate unit and any contribution to the luminescence made by the Cu-alkynyl network in solution is masked by the more intense bands of the Cu-hfac rings.

Conclusion

Despite the very different structures and bonding modes in the cores of the Cu$_{16}$, Cu$_{20}$ and the earlier reported Cu$_{18}$ and Cu$_{26}$ clusters their electronic properties and NMR spectra are remarkably similar. The facility with which the different clusters can be isolated under very similar preparative conditions suggests that differences in the nature of the alkynes may be responsible for the formation of different core networks. As noted previously, as it is the alkyne which functions as the bridging ligand while the hfac 'caps' the exterior, increasing the alkynyl : hfac stoichiometry should lead to larger clusters. This rule of thumb applies with straight chain alkynes, *e.g.* [Cu$_{18}$-(hfac)$_{10}$(C≡CBu^n)$_8$] *cf.* [Cu$_{26}$(hfac)$_{11}$(C≡CPr^n)$_{15}$]. When a bulkier alkyne *e.g.* Bu^{t}C≡CH is used in this preparation the ability to function as a bridging unit in the core may be inhibited; No alkynyl π-bridges between Cu atoms (type **D**, Fig. 3) are observed in [Cu$_{16}$(hfac)$_8$(C≡CBu^t)$_8$]. The benzylacetylene ligand allows such μ-π-bridges to form, but possibly the steric factors associated with the benzene rings limits the efficiency with which these alkynes which can function as bridging units in the core.

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