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$[Cu_{18}(hfac)_{10}(C\equiv CC_4H^n_9)_8]$; Crystal structure of a novel luminescent cage compound with a "triple copper sheet" structural motif

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The synthesis, crystallography and solution luminescence properties of $[Cu_{18}(hfac)_{10}(C\equiv CC_4H^n_9)_8]$ are reported.

The field of Cu(I) alkynyl cluster chemistry is attracting considerable interest because the specific physicochemical properties of such compounds, *e.g.* non-linear optics,[1,2] luminescence,[1,3,4] and molecular conductivity,[5] may lead to commercial applications in optoelectronic devices.[1,2] We have recently developed simple procedures for the synthesis of $[Cu_{x+y}(hfac)_x(C\equiv CR)_y]$ type clusters, such as $[Cu_{26}(hfac)_{11}(C\equiv CC_3H^n_7)_{15}]$.[6] During the preparation of a related Cu_{26}-cluster, $[Cu_{26}(hfac)_{12}(C\equiv CC_4H^n_9)_{14}]$, the presence of a minor product was observed. A method to purify this orange solid material, involving fractional crystallisations from *n*-hexane, has been developed† and this material has been crystallographically characterised (Fig. 1).[7]

The molecule crystallised in a non-centrosymmetric space group and appears to be racemically twinned within the crystal with a refined Flack parameter of 0.517(6).[8] The Bravais lattice is orthorhombic, space group: $Pca2_1$, the asymmetric unit containing one complete molecule of $[Cu_{18}(hfac)_{10}(C\equiv CC_4H^n_9)_8]$. The Cu ions are contained within three parallel planes, an "upper" and "lower" plane or layer, each containing seven metal ions and an intermediate "spacer" plane of four linear two coordinate Cu ions with η^1_σ-$(C_4H_9C\equiv C)_2$ ligation. These three parallel planes specify the cluster's larger (lateral) dimensions, whilst their perpendicular defines its smallest dimension (thickness). The five peripheral Cu ions in each of the "upper" and "lower" sheets are capped by hfac ligands and the central two Cu ions are interlinked into the main body of the cluster *via* four bridging hexynyl ligands. These alkynyl (L) ligands possess a variety of coordination/bridging modes[9] including μ_3-$(\eta^1_\sigma)_2,\eta^2_\pi$ (3 × L), μ_4-$(\eta^1_\sigma)_2,(\eta^2_\pi)_2$ (1 × L), μ_4-$(\eta^1_\sigma)_3,\eta^2_\pi$ (3 × L), and μ_5-$(\eta^1_\sigma)_3,(\eta^2_\pi)_2$ (1 × L). The core is comprised of two pairs of trigonal planar η^1_σ-$(^nC_4H_9C\equiv C)_3Cu$ units from the "upper" and "lower" Cu-planes in an eclipsed apical conformation with two alkynyl ligands directly linking Cu(2) ··· Cu(5) and Cu(3) ··· Cu(4), *via* μ-$(\eta^1$-$C_4H_9C\equiv C)$ bridging motifs. These four hexynyl ligands are also bonded to Cu(1) and Cu(6) in the central plane, thus providing two of the linear η^1_σ-$(C\equiv C)_2Cu$ "spacer" units. The two other $(^nC_4H_9C\equiv C)_2Cu$ spacer units involve Cu(9) and Cu(14), these connect Cu(2) [2.504(1) Å] to Cu(3) [2.516(1) Å] and Cu(4) [2.473(1) Å] to Cu(5) [2.499(1) Å] respectively, making outwardly directed contact angles of, Cu(2) ··· Cu(9) ··· Cu(3): 80.62(2)° and Cu(4) ··· Cu(14) ··· Cu(5): 79.73(2)°. The Cu(1–6) core is arranged in a distorted octahedron with two distances, Cu(2) ··· Cu(3) [3.247(1) Å] and Cu(4) ··· Cu(5) [3.187(1) Å], significantly longer than the remainder [average, 2.61(1) Å], defining the spacing between the "upper" and "lower" sheets. Numerous Cu ··· Cu distances within the cluster, are less than the sum of the van der Waals radii for two Cu(I) ions (2.8 Å)[10] thus indicating the possible presence of $[d^{10}$–$d^{10}]$ closed shell cuprophilic interactions.[11–13] The majority of these Cu ··· Cu close contact pairs involve one of the sterically "open" η^1_σ-$(C\equiv C)_2Cu$ moieties; these permit a proximal distribution of other Cu ions about them.

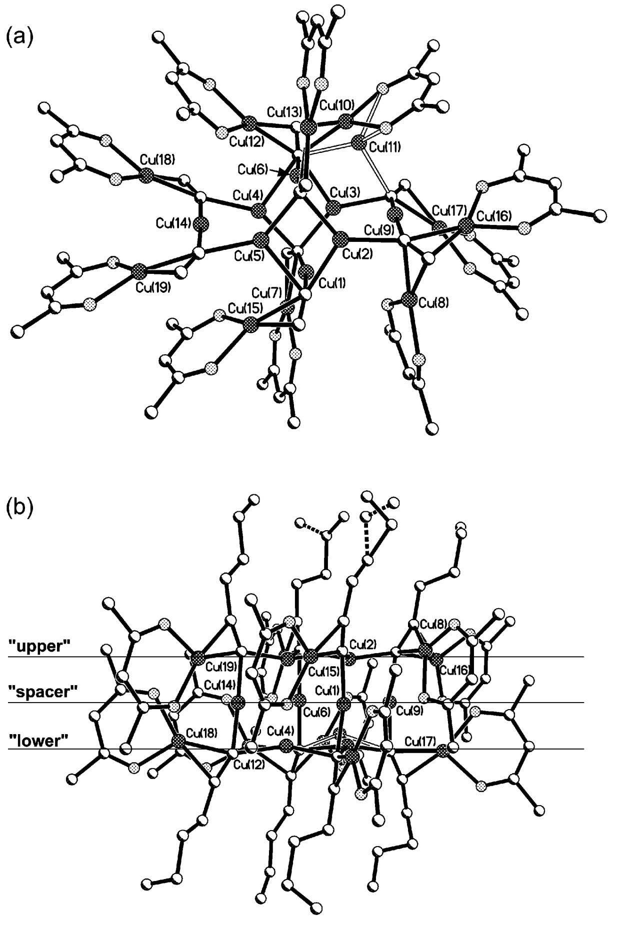

Fig. 1 Plots of the $[Cu_{18}(hfac)_{10}(C\equiv CC_4H^n_9)_8]$ molecule with Cu ions labelled. (a) Apical view with the $-C_4H_9$ alkyl chains absent. (b) Lateral view indicating "upper" (Cu_7), "spacer" (Cu_4), and "lower" (Cu_7) Cu-planes. For clarity, all possible Cu ··· Cu bonds, and the H and F atoms are omitted. Hollow bonds indicate the lower occupancy site, Cu(11), of the disordered copper ion Cu(10/11).

The 10 × hfac ligands are O_2-bidentate and arranged in a toroidal fashion, capping the periphery of the "upper" and "lower" Cu_7-sheets. The C_4H_9 alkyl chains of the hexynyl ligands are orientated along the axial direction in a $[4]^{\Uparrow} + [4]_{\Downarrow}$ arrangement, displaying a strikingly anisotropic distribution relative to the hfac ligands similar to that of $[Cu_{26}(hfac)_{11}(C\equiv CC_3H^n_7)_{15}]$.[6] One Cu ion (labelled Cu(10)/Cu(11)) is disordered over two sites in the ratio 0.67 : 0.33, separated by 0.83(1) Å, with the major occupant being $O_2(\eta^2_\pi$-$C\equiv C)_1$ ligated and the minor $O_2(\eta^1_\pi$-$C\equiv C)_2$. Most Cu–ligand bond distances [average values, Cu–O: 1.97(1) Å, Cu-$(\eta^2_\pi$-$C\equiv C)$: 2.01(1) Å, Cu_{linear}-$(\eta_\sigma{}^1$-$C\equiv C)$: 1.91(1) Å] are well within the limits typically observed for these bond types with Cu(I).[6,14,15] The trigonal planar $(C\equiv C)_3Cu$ units [Cu(2–5)] each possess one "long" [2.122(3)–2.291(3) Å] Cu–C bond.

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Table 1 Summary of UV-vis absorptions [*n*-hexane, λ/nm (ε/M^{-1} cm^{-1})] and luminescence data for [$Cu_{18}(hfac)_{10}(C{\equiv}CC_4H_9^n)_8$] (*n*-hexane, 5.49 × 10^{-5} M, λ/nm). The emission bands are aligned with their corresponding UV-vis electronic/excitation absorptions [* solvent Raman bands]

UV-Vis absorption	Excitation λ_{em}, 400 nm	Emission λ_{ex}, 280 nm	Emission λ_{ex}, 330 nm	Emission λ_{ex}, 340 nm
231sh. (99420)	**293**	**344**		
305 (89480)	**336**		**367, 382**	**367, 382**
437br.sh. (8822)				
	357*, 379*	307*	367*	379*

The observation, by Yam *et al.*,[1,3,4] of luminescence properties in multinuclear Cu(I)-alkynyl systems, with the photoactive excited states reported as possessing substantial [Cu(I)–C≡CR] CT character, prompted us to investigate the photophysical properties of [$Cu_{18}(hfac)_{10}(C{\equiv}CC_4H_9^n)_8$] (see Table 1). Its electronic spectrum possesses three major absorption envelopes, all overlapping, two intense bands at high energy [231(sh), 305 (λ_{max}) nm] which have been provisionally assigned to internal transitions (π⟶π*, n⟶π*) in the hexynyl and hfac ligands. The third band exists as a broad asymmetric envelope of lower intensity [437 nm (8822 M^{-1})]. This has been tentatively assigned to overlapping (η_π^2-C≡C)–Cu(I) CT and (η_σ^1-C≡C)–Cu(I) CT transitions, the broad nature of the absorption being due to the variety of types of ($^nC_4H_9C{\equiv}C$)Cu coordination that exists in this system. The excitation spectrum, recorded at an emission wavelength of 400 nm, displays two bands at 293 and 336 nm, responsible for the luminescence properties of this system. The 293 nm-centred excitation leads to an intense emission at 344 nm. The 336 nm excitation leads to a much weaker emission envelope (partially obscured by a solvent Raman band) containing a minimum of two peaks centred at 367 and 382 nm, confirmed by Gaussian spectral deconvolution [Fig. 2 (inset)], which are indicative of vibronic fine structure. The relative weakness of this emission suggests that the emitting state has an efficient non-radiative decay channel. For example, the emission may result from a long-lived excited state (*i.e.* a spin-forbidden transition) which would be subject to collisional deactivation by solvent molecules.

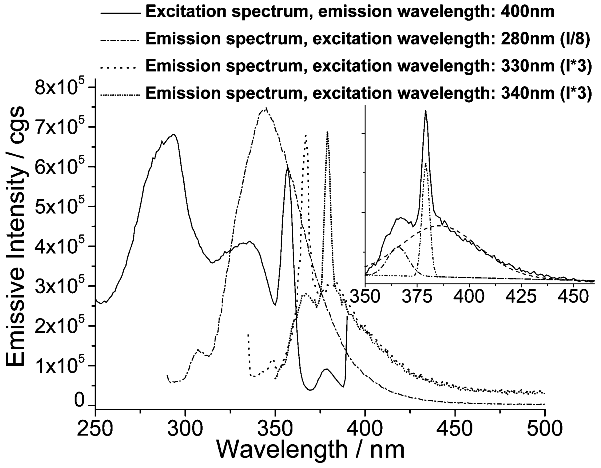

Fig. 2 Overlaid excitation and emission solution spectra of [$Cu_{18}(hfac)_{10}(C{\equiv}CC_4H_9^n)_8$] in *n*-hexane (5.49 × 10^{-5} M) at RT. **Inset:** Detail of emission spectrum at excitation wavelength of 340 nm and its Gaussian deconvolution fit with three peaks at 365.8, 379.2 (solvent Raman band), and 385.9 nm respectively.

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Notes and references

† Experimental details. Schlenk line techniques were employed using anhydrous solvents and dry nitrogen. 1-Hexyne and 1,1,1,5,5,5-hexafluoropentan-2,4-dione (hfacH) were degassed by three freeze/vacuum/thaw cycles.

[$Cu_{18}(hfac)_{10}(C{\equiv}CC_4H_9^n)_8$]. Into 1-hexyne (8.5 cm^3) was placed Cu_2O (1.64 g, 11.46 mmol) and anhydrous $MgSO_4$ (2.0 g, 16.6 mmol) forming a bright red suspension. hfacH (2.50 cm^3, 17.66 mmol) was added dropwise to the suspension, the flask was wrapped with Al-foil and the mixture stirred at RT for 18 h, cannula-filtered and the solid residues washed with three portions of *n*-hexane (10 cm^3). The yellow–green filtrate and washings were combined, evaporated to dryness yielding a viscous dark red oil which was heated at 65 °C *in vacuo* for 1 h. This material was recrystallised from hot *n*-hexane (15 cm^3) initially forming red crystals and then a small number of orange crystals. The liquor was decanted and then cooled to 4 °C for 5 days causing a dense mass of orange crystals to deposit together with a few red crystals. The supernatant was decanted, discarded and the crystals recrystallised from hot *n*-hexane (12 cm^3) yielding solely bright orange crystals, these were collected and dried *in vacuo*. Yield: 0.613 g (9%). Anal. calc. for $C_{98}H_{82}Cu_{18}F_{60}O_{20}$: C, 30.47; H, 2.14. Found: C, 30.57; H, 2.19%. IR (KBr disk, cm^{-1}): 3134, 2964, 2936, 2876, 1922, 1673, 1639, 1554, 1528, 1460, 1384, 1345, 1255, 1208, 1146, 1097, 944, 795, 743, 671, 586, 527.

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