Synthesis, photophysics and crystal structures of hexanuclear copper(i) and silver(i) acetylide complexes

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The luminescent complexes $[\mathrm{M_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4C{\equiv}C\text{-}}p\mathrm{)M_3(\mu\text{-}Ph_2PCH_2PPh_2)_3][BF_4]_4}$ are synthesized by the reaction of $[\mathrm{M_2(\mu\text{-}Ph_2PCH_2PPh_2)_2(MeCN)_2}]^{2+}$ and 1,4-diethynylbenzene in the presence of Bu^{n}Li in thf (M = Cu 1, Ag 2); X-ray crystal structures of both are determined.

The highly conjugated polyynes and their transition-metal complexes have attracted enormous attention as precursors for non-linear optical materials and rigid-rod molecular wires.[1] Recently, we synthesized the first luminescent binuclear Re$^{\mathrm{I}}$ organometallics with a rigid-rod acetylide backbone.[2] With our recent interest in polynuclear Cu$^{\mathrm{I}}$ and Ag$^{\mathrm{I}}$ acetylide complexes,[3] we believe that these complexes would be ideal building blocks for the design of luminescent rigid-rod oligomers. Here, we report the first synthesis of two novel luminescent diyne-bridged hexanuclear copper(i) and silver(i) complexes $[\mathrm{Cu_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4C{\equiv}C\text{-}}p\mathrm{)Cu_3(\mu\text{-}Ph_2PCH_2PPh_2)_3][BF_4]_4}$ **1** and $[\mathrm{Ag_3(\mu\text{-}Ph_2PCH_2PPh_2)_3(\mu_3\text{-}\eta^1\text{-}C{\equiv}CC_6H_4C{\equiv}C\text{-}}p\mathrm{)Ag_3(\mu\text{-}Ph_2PCH_2PPh_2)_3][BF_4]_4}$ **2**; both of which contain two triangular M$^{\mathrm{I}}_3$ units linked *via* an extended conjugated diyne backbone.

Bu^{n}Li was added at room temperature to a solution of 1,4-diethynylbenzene[4] in predried, degassed thf under an inert atmosphere of nitrogen; a solid sample of $[\mathrm{Cu_2(\mu\text{-}dppm)_2(MeCN)_2][BF_4]_2}$[5] was then added and stirred at room temp. for 24 h. After evaporation to dryness, the resulting solution was extracted with $\mathrm{CH_2Cl_2}$. Subsequent diffusion of diethyl ether into the concentrated solution gave **1** as air-stable yellow crystals. Complex **2** was obtained as air-stable pale yellow crystals by a similar method except that $[\mathrm{Ag_2(\mu\text{-}dppm)_2(MeCN)_2][BF_4]_2}$[6] was used. Both **1** and **2** have been characterized by elemental analyses, ^{1}H NMR, IR and Raman spectroscopy.† The X-ray crystal structures of **1** and **2** have also been determined.‡

A perspective drawing of the complex cation of **1** with atomic numbering is shown in Fig. 1. The complex cation of **1** consists of two triangular arrays of copper atoms with a dppm ligand bridging each edge to form two roughly planar $\mathrm{Cu_3P_6}$ cores bridged by a 1,4-diethynylbenzene unit to form a dumb-bell shaped structure. The Cu···Cu distances, which are comparable to those found in the related monocapped systems,[3*a*,*c*,7,8] are suggestive of at best only very weak Cu···Cu interactions. The bridging mode of the alkynyl group is asymmetric and the C≡C bond length is typical of metal–acetylide σ bonding. It is interesting that the phenyl ring of the acetylide unit which sits in the middle of the complex is almost parallel to the two phenyl rings [C(51)–(56), C(51*)–(56*)] of the dppm units, one on each of the triangular core, respectively, indicative of the presence of π-stacking interactions. The complex cation of **2** is isostructural to **1** and similar π-stacking interactions are observed.

The absorption spectra of **1** and **2** display strong absorptions in the UV region at *ca*. 258–324 nm, tentatively assigned as ligand-localized transitions. Longer wavelength absorptions appear as vibronically structured bands at *ca*. 370–416 nm for **1** and *ca*. 324–364 nm for **2** in $\mathrm{CH_2Cl_2}$, with vibrational progressional spacings of *ca*. 1475–1500 cm^{-1}, typical of $\nu(\mathrm{C}\overset{\dots}{-}\mathrm{C})$ stretching modes of the aromatic ring in the excited state. Excitation of a solid sample of complex **1** at $\lambda > 350$ nm both at 77 K and room temp. produces intense yellow–orange luminescence. The room-temp. solid-state emission spectrum shows an intense band at *ca*. 583 nm, which is also vibronically structured with progressional spacings of *ca*. 1500–1520 cm^{-1}, characteristic of the aromatic $\nu(\mathrm{C}\overset{\dots}{-}\mathrm{C})$ stretch. Upon cooling to 77 K, the emission bands become better resolved. Similar emission bands are observed in fluid solution. Excitation of a solid sample of **2** at $\lambda > 350$ nm both at 77 K and room temp. give intense green–yellow luminescence. The solid-state emission spectrum also shows an intense vibronically structured band at *ca*. 513 nm at both room temp. and 77 K (Table 1). The excitation spectra of both **1** and **2** show vibronically structured bands at *ca*. 360–420 and 320–362 nm, respectively, which coincide with those of their respective absorption spectra. The excitation and emission spectra of **2** in degassed dichloromethane at 298 K are shown in Fig. 2.

It is interesting that both the absorption and emission bands of **1** occur at lower energy than those of **2**. A possible assignment for the origin of the emission involves emissive states derived from ligand-to-metal charge transfer (acetylide-to-metal

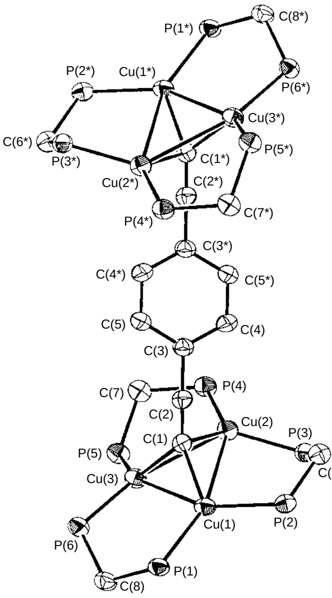

Fig 1 Perspective drawing of the complex cation of **1** with atomic numbering scheme. Hydrogen atoms and phenyl rings have been omitted for clarity. Thermal ellipsoids are shown at the 40% probability level. Selected bond lengths (Å) and angles (°): **1** C(1)–C(2) 1.223(9), C(1)–Cu(1) 1.996(7), C(1)–Cu(2) 2.101(7), C(1)–Cu(3) 2.042(7), Cu(1)···Cu(2) 3.243(1), Cu(1)···Cu(3) 2.862(2), Cu(2)···Cu(3) 2.885(1); Cu(1)–C(1)–C(2) 143.3(7), Cu(2)–C(1)–C(2) 87.5(5), Cu(3)–C(1)–C(2) 125.1(6), Cu(1)–Cu(2)–Cu(3) 55.31(3), Cu(2)–Cu(1)–Cu(3) 55.98(3), Cu(1)–Cu(3)–Cu(2) 68.71(3). **2** C(1)–C(2) 1.24(2), C(1)–Ag(1) 2.28(1), C(1)–Ag(2), 2.29(1), C(1)–Ag(3) 2.23(1), Ag(1)···Ag(2) 3.338(1), Ag(1)···Ag(3) 3.163(1), Ag(2)···Ag(3) 3.079(1); Ag(1)–C(1)–C(2) 120.6(9), Ag(2)–C(1)–C(2) 114.9(9), Ag(3)–C(1)–C(2) 140.2(10), Ag(1)–Ag(2)–Ag(3) 58.89(3), Ag(2)–Ag(1)–Ag(3) 56.46(3), Ag(1)–Ag(3)–Ag(2) 64.65(3).

LMCT) transition mixed with d–s character. The red shift in the 77 K solid-state emission energy of *ca*. 0.28 eV from **2** to **1** is comparable to the value of 0.31 eV reported for the related hexanuclear Ag^I and Cu^I thiocarbamate clusters, $[Ag_6(mtc)_6]$ and $[Cu_6(mtc)_6]$ (mtc = di-*n*-propylmonothiocarbamate), where an origin of mixed d $\longrightarrow$ s and LMCT character has been suggested.[9] Besides, a similar red shift in emission energy (*ca*. 0.27 eV) on going from Ag^I to Cu^I chalcogenido clusters has been reported,[10a–c] in which a mixed d $\longrightarrow$ s/LMCT origin has also been suggested and is supported by molecular orbital calculations.[10d,e] Another possible origin for the observed red shift in energy from **2** *cf*. **1** involves states derived from metal-to-ligand charge transfer [MLCT d(M) $\longrightarrow$ π^*(acetylide)] transition. As Cu^I is much more easily oxidized, given the higher energy of the Cu^I 3d orbitals relative to those of the Ag^I 4d orbitals,[11] the MLCT transition for Cu^I should also occur at lower energy than that for Ag^I. In view of the fact that the ionization energy of $Ag^+(g)$ is nearly 10^4 cm^{-1} larger than that for $Cu^+(g)$,[11] an assignment of the emissive state as derived from a MLCT transition for the small energy shift observed from **2** to **1** is unlikely. The long lifetime of the emissive state in the μs range is probably suggestive of triplet origin. However, the possibility of an involvement of an intraligand excited state of 1,4-diethynylbenzene should not be overlooked given the unusually long lifetime of the emissive state and the low-lying π^* orbital energy of the diynyl unit. Therefore, it is likely that the low-energy emission is derived from states of LMCT parentage mixed with a metal-centred $nd^9(n+1)s^1$ state, with large intraligand $\pi\pi^*$ character.

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Table 1 Photophysical data for complexes **1** and **2**

Complex	Medium (*T*/K)	Absorption λ_{max}/nm (10^{-4} ε_{max}/dm^3 mol^{-1} cm^{-1})	Emission λ_{em}/nm (τ_o/μs)
1	CH_2Cl_2 (298)	260(sh) (8.32), 294(sh) (4.41), 370(sh) (1.69), 390 (2.32), 416 (2.46)	596 (40)
	Solid (298)		583 (222)
	Solid (77)		582
	EtOH–MeOH (v/v 1 : 4) glass (77)		579
2	CH_2Cl_2 (298)	258(sh) (5.52), 324 (1.40), 340 (1.47), 364 (1.64)	515 (426)
	Solid (298)		513 (351)
	Solid (77)		515
	EtOH–MeOH (v/v 1 : 4) glass (77)		510

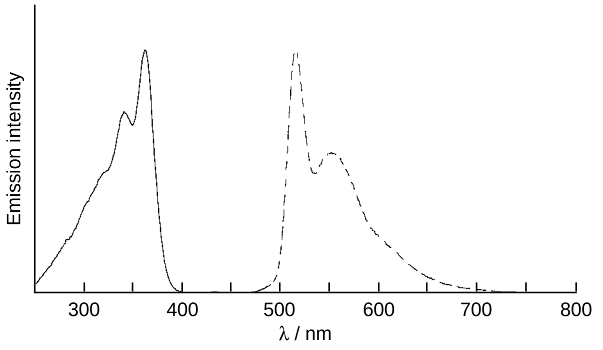

Fig. 2 Excitation (—) and emission (---) spectra of **2** in degassed CH_2Cl_2 at 298 K

Footnotes

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† **1**: yield, 53%. ^1H NMR (CD_2Cl_2), δ 3.4 (m, 6 H, CH_2), 3.6 (m, 6 H, CH_2), 6.8–7.4 (m, 120 H, PPh_2), 7.5 (s, 4 H, Ph). IR(Nujol) ν/cm^{-1}: 1062s [ν(B–F)]. Raman (solid sample) ν/cm^{-1}: 1955s [ν(C≡C)]. Satisfactory elemental analysis. **2**: yield, 46%. ^1H NMR ([$^2H_6$]acetone), δ 3.8 (m, 6 H, CH_2), 3.9 (m, 6 H, CH_2), 7.0–7.6 (m, 120 H, PPh_2), 7.7 (s, 4 H, Ph). IR(Nujol) ν/cm^{-1}: 1054s [ν(B–F)]. Raman (solid sample) ν/cm^{-1}: 2015s [ν(C≡C)]. Satisfactory elemental analysis.

‡ *Crystal data*: for **1**: $C_{160}H_{136}B_4Cu_6F_{16}P_{12}\cdot 2CH_2Cl_2$; $M = 3328.88$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.134(4)$, $b = 22.139(6)$, $c = 13.783(3)$ Å, $\alpha = 106.62(2)$, $\beta = 99.28(3)$, $\gamma = 102.78°$, $U = 3912(2)$ $Å^3$, $Z = 1$, $D_c = 1.413$ g cm^{-3}, μ(Mo-Kα) = 10.61 cm^{-1}, $F(000) = 1698$, $T = 301$ K. Convergence for 864 variable parameters by least-squares refinement on F with $w = 4\ F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.030F_o^2)^2]$ for 6585 reflections with $I > 3\sigma(I)$ was reached at $R = 0.064$ and $R_w = 0.087$.

For **2**: $C_{160}H_{136}Ag_6B_4F_{16}P_{12}\cdot 4CH_2Cl_2$; $M = 3764.67$, triclinic, space group $P\bar{1}$ (no. 2), $a = 14.393(3)$, $b = 22.346(5)$, $c = 14.323(5)$ Å, $\alpha = 95.38(2)$, $\beta = 95.07(2)$, $\gamma = 106.06(2)°$, $U = 4375(2)$ $Å^3$, $Z = 1$, $D_c = 1.429$ g cm^{-3}, μ(Mo-Kα) = 9.52 cm^{-1}, $F(000) = 1890$, $T = 301$ K. Convergence for 946 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2\ (F_o^2) = [\sigma^2(I) + (0.016F_o^2)^2]$ for 9594 reflections with $I > 3\sigma(I)$ was reached at $R = 0.073$ and $R_w = 0.102$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/448.

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