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The first luminescent tetranuclear copper(I) μ_4-phosphinidene complex†

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The first luminescent tetranuclear copper(I) phosphinidene complex $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-PPh})](BF_4)_2$ has been synthesized and isolated; the red-light emitting properties and air-stability of the complex in the solid state may render great potential for this new class of compounds in the future development of semiconducting luminescence materials and applications in LED technology.

The recent growth in interest in the chemistry of transition metal–pnictogenide complexes has been prompted in part by the potential of utilizing such compounds as precursors of binary pnictogenides in the development of electronic and optical materials.[1] With different particle size, the luminescence and optical properties of the transition metal–pnictogenides may vary dramatically due to the quantum size effect.[2] Therefore one of the important aspects in this field is to prepare particles or synthesize model complexes with a controllable and uniform size. In view of this, together with our recent efforts on the syntheses and isolations of a number of polynuclear coinage metal chalcogenide complexes with a d^{10} electronic configuration,[3] we believe that an exploration into the related phosphinidene complexes might give rise to new classes of soluble molecular materials of uniform size, with easily tunable luminescence properties *via* the participation of different ancillary ligands. To the best of our knowledge, phosphinidene complexes of d^{10} transition metals are extremely rare.[4,5] Herein, is described the first report on the isolation, characterization and X-ray crystal structure of a novel red-light emitting tetranuclear copper(I)–phosphinidene complex, $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-PPh})](BF_4)_2$ **1** [dppm = bis(diphenylphosphino)methane], which is stable to air in the solid state and highly soluble in common organic solvents. Its photophysical properties have also been investigated.

Reaction of $[Cu_2(\mu\text{-dppm})_2(MeCN)_2](BF_4)_2$[6] with $PhPH_2$ and $Na(acac)\cdot H_2O$ (acac = acetylacetonate) in THF under nitrogen gave an orange precipitate. Recrystallization from dichloromethane–diethyl ether afforded **1** as air-stable orange-red crystals in 80% yield. The formulation of **1** was confirmed by elemental analyses, positive FAB-MS, ^1H and ^{31}P NMR spectroscopy.‡ The solid state structure was established by X-ray crystallography.§

Fig. 1 shows the perspective drawing of the complex cation of **1**. The four copper atoms are almost coplanar and form a rectangular array, with the four bridging dppm ligands arranged in a saddle-like configuration. The Cu–Cu distances range from 2.8225(9) to 3.4451(1) Å, and show no significant $Cu^I\cdots Cu^I$ interactions. The phosphinidenic phosphorus sits at the apex of the distorted square-pyramid and quadruply bridges the four copper atoms, with projection of *ca.* 0.70 Å above the idealized Cu_4 plane. The plane of the phenyl ring on the phosphinidene is perpendicular to the Cu_4 plane and has an orientation that bisects the two longer Cu–Cu edges, Cu1–Cu4 and Cu2–Cu3, so as to minimize the steric hindrance experienced by the phenyl rings on the phosphinidene and the two dppm ligands that were folded upwards. This is also in accordance with the observed elongation of the Cu–Cu long edges and the shortening of the short edges when compared to the isoelectronic but less sterically demanding chalcogenide counterparts, $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-S})](PF_6)_2$ [3.128(1), 2.869(1) Å] and $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-Se})](PF_6)_2$ [3.271(4), 2.908(4) Å].[3c,d] The Cu–P(phosphinidene) bond distances of 2.2811(1)–2.3230(1) Å are comparable to other Cu^I–μ_4-PR systems, such as $[Cu_{24}\{P(Me_2(Pr^iMe_2C)Si)\}_{12}]$ [2.226(3) Å] and $[Cu_{18}(PPh)_4(PPh_2)_{10}(PHPh_2)_3]$ [2.272(2)–2.449(2) Å].[4] All the Cu–P(dppm) bond distances are typical of those reported in other copper(I)–dppm systems.[7] It is of note that all Cu–P(dppm) bonds on the same side as the phosphinidene moiety are longer than those on the other side. This is simply a consequence of the steric requirements for the accommodation of the phosphinidene and the dppm ligands on the same side of the Cu_4 rectangle.

The ^1H NMR spectrum of **1** in CD_2Cl_2 at ambient temperature shows four broad methylene proton signals with equivalent integrals, indicative of the absence of a flipping motion for dppm and the rotation of the phosphinidene group. This is different from the situation in $[M_4(\mu\text{-dppm})_4(\mu_4\text{-E})]^{2+}$ (M = Cu, Ag; E = S, Se, Te), where flipping motions of the dppm ligands occurs and only one methylene signal has been observed.[3c–e] The $^{31}P\{^1H\}$ NMR spectrum shows the unresolved phosphinidene P signal at δ −94.97, a much more downfield environment compared to the structurally related AuI–phosphinidene complexes, $[2,4,6\text{-}Bu^t_3C_6H_2P(AuPPh_3)_4](BF_4)_2$ (δ −47.69) and $[2\text{-}MeC_6H_4P(AuPPh_3)_4](BF_4)_2$ (δ −54.6).[5]

The electronic absorption spectrum of **1** in CH_2Cl_2 shows a low-energy absorption band at *ca.* 466 nm (Fig. 2). The electronic absorption spectral data are summarized in Table 1. With reference to previous spectroscopic work on the related metal chalcogenido systems,[3] the low energy absorption band at 466 nm, which is absent in the copper(I) precursor complex, is likely to be originated from the [P(phosphinidene) → Cu]

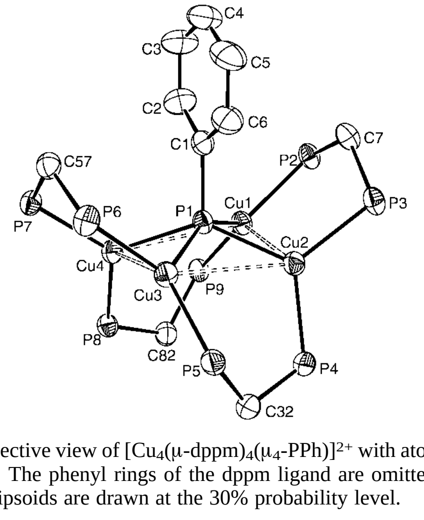

Fig. 1 Perspective view of $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-PPh})]^{2+}$ with atomic numbering scheme. The phenyl rings of the dppm ligand are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

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† Electronic supplementary information (ESI) available: full crystal structure determination details. See http://www.rsc.org/suppdata/cc/b1/b101284n/

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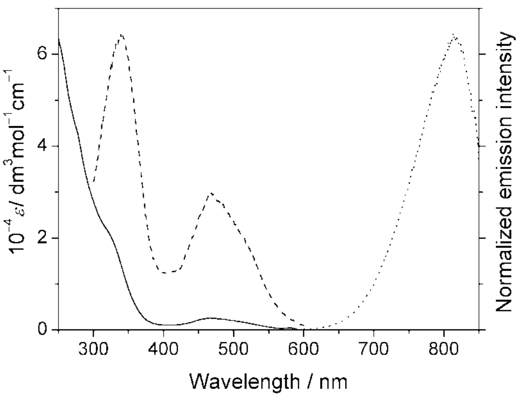

Fig. 2 Electronic absorption (——), emission (-----) and excitation (monitored at 816 nm) (······)·spectra of **1** in CH_2Cl_2 at 298 K.

Table 1 Photophysical data for **1**

$\lambda_{abs}{}^{a}$/nm (ε/dm^3 mol^{-1} cm^{-1})	Medium (T/K)	$\lambda_{em}{}^{c}$/nm	τ_o/μs
268 (sh)[b] (49370), 316 sh[b] (23460), 466 (3480)	Solid (298)	718	8.3 ± 0.2
	Solid (77)	754	550 ± 50
	CH_2Cl_2 (298)	816	2.0 ± 0.1
	CH_2Cl_2 (77)	825	330 ± 30

[a] In CH_2Cl_2 at 298 K. [b] The absorption shoulders were determined from the derivatives of the UV–VIS absorption spectra. [c] Corrected for photomultiplier tube response.

ligand-to-metal charge-transfer (LMCT) transition. An assignment of such low-energy bands to intraligand IL (phosphinidene) transitions is unlikely as the related gold(I) phosphinidene complex, $[2\text{-MeC}_6H_4P(AuPPh_3)_4](BF_4)_2$,[5b] is reported to be colourless, indicating the absence of low-energy absorption in this region. The high-energy band at 268 nm is attributed to the intra-ligand transition of dppm.

Excitation of **1** in the solid state and in fluid solutions at $\lambda \approx$ 500 nm results in intense long-lived red luminescence (Table 1). Excitation bands at *ca.* 339 and 469 nm were observed upon monitoring the emission at 816 nm (Fig. 2). The close resemblance of the excitation spectrum to the electronic absorption spectrum is suggestive of an emission origin derived from the [P(phosphinidene) $\rightarrow$ Cu] LMCT transition. The observed lifetime in the microsecond range indicates the spin-forbidden nature of the emission, that is tentatively assigned to be originated predominantly from the triplet state derived from the [P(phosphinidene) $\rightarrow$ Cu] LMCT transition that mixed with a metal-centred (d–s/d–p) Cu^I state. Such an assignment is based on the fact that the phosphinidene group, being isoelectronic with and similar to the unsubstituted chalcogenides, is a good σ-donor. The red-shift in the emission energies upon lowering the temperature is supportive of such an assignment as it can readily be rationalized by the shrinking of the Cu_4 skeleton, which lowers the energy of the sσ acceptor orbitals derived from the overlap of the 4s orbitals of copper. Assignment based on similar grounds has been reported on the related systems with d^8–d^8 metal–metal interactions.[8]

The present work demonstrates a facile, high-yield synthesis towards soluble luminescent copper(I) phosphinidene complexes. This may, in one way or the other, open up new avenues to the chemistry of polynuclear copper(I) complexes by utilizing the $[Cu_4(dppm)_4]PR$ unit as the building block for higher nuclearity copper(I) complexes and clusters, through various functionalizations on the organic R group. Examples of polynuclear gold(I) aggregates made by using this approach have been illustrated by Schmidbaur *et al.*[9] The present system may also serve as a potential precursor to advanced luminescent materials for applications in the electro-luminescent technology; the emission colour of which could be readily fine-tuned by employing various R groups that have different electron-donating/withdrawing ability.[10]

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Notes and references

‡ $[Cu_4(\mu\text{-dppm})_4(\mu_4\text{-PPh})](BF_4)_2$ **1**: elemental analyses: calc. for **1**$\cdot 0.5CH_2Cl_2$ (found): C 60.45 (60.66), H 4.48 (4.51)%; positive FAB-MS: *m/z* 1987 $[M - BF_4]^+$, 1602 $[M - dppm - BF_4]^+$, 950 $[M - 2BF_4]^{2+}$; ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 2.51 (m, 2H, CH_2), 2.87 (m, 2H, CH_2), 3.31 (m, 2H, CH_2), 3.50 (m, 2H, CH_2), 6.30–7.71 (m, 85H, Ph); $^{31}P\{^1H\}$ NMR (202 MHz, CD_2Cl_2, 298 K): δ −10.81 (m, I = 4, dppm), −12.96 (m, I = 4, dppm), −94.97 (m, I = 1, phosphinidene).

§ *Crystal data* for **1**: $C_{106}H_{93}B_2Cu_4F_8P_9\cdot 2CH_2Cl_2$: M_r = 2243.17, monoclinic, space group *Cc* (no. 9), a = 14.456(2), b = 28.797(3), c = 25.340(3) Å, β = 91.27(2)°, V = 10546(2) Å^3, T = 301 K, Z = 4, D_c = 1.413 g cm^{-3}, μ(Mo-Kα) = 1.094 mm^{-1}, 31947 reflections measured, 17709 unique (R_{int} = 0.0401) which were used in all calculations. The final $R(F^2)$ was 0.0513 [$I > 2\sigma(I)$]. CCDC 154244. See http://www.rsc.org/suppdata/cc/b1/b101284n/ for crystallographic data in .cif or other electronic data format.

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