

Synthesis and Luminescent Properties of a Novel Tetranuclear Copper(I) Cluster containing a μ_4 -Sulfur Moiety. X-Ray Crystal Structure of $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-S})](\text{PF}_6)_2 \cdot 2\text{Me}_2\text{CO}$ [dppm = bis(diphenylphosphino)methane]

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A novel tetranuclear copper(I) cluster containing a μ_4 -sulfur bridge has been synthesized and characterized crystallographically; long-lived luminescence is observed both in the solid state and in fluid solutions.

In view of the unusual stereochemistry and various bonding modes of unsubstituted sulfur ligand, there has been an increasing interest in soluble metal-sulfur complexes. Interest in these metal-sulfur cluster compounds of high nuclearity has also been stimulated by studies on functional models of metal-sulfur redox proteins and in general by synthetic, structural, theoretical and catalytic research in the field of organometallic cluster chemistry.¹ However, sulfur bridges of type D mode (μ_4 -bridging), with three possible alternatives, are all rather rare.² Examples of type D1 include

$[\text{Co}_4\text{S}_2(\text{CO})_{10}]$,³ $[\text{Co}_7(\mu_4\text{-S})_3(\mu_3\text{-S})_3(\text{PPh}_3)_4\text{Br}_{1.5}\text{Cl}_{1.5}]$,³ $[\text{Mo}_4(\text{NO})_4\text{S}_{13}]^{4-}$,⁴ $[\text{Ni}_9(\mu_4\text{-S})_3(\mu_3\text{-S})_6(\text{PEt}_3)_6]^{2-}$,⁵ and those of carbonyl ruthenium sulfido clusters.⁶ In this communication, we describe the synthesis and luminescent properties of the first example of tetranuclear copper cluster containing a μ_4 -sulfido moiety (type D1), which has been characterized by X-ray crystallography.

Reaction of $[\text{Cu}_2(\mu\text{-dppm})_2(\text{MeCN})_2](\text{PF}_6)_2$ and Na_2S in acetone-methanol, followed by vapour diffusion of diethyl ether gave $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-S})](\text{PF}_6)_2$ as air stable yellow

crystals in high yield; the identity of which has been characterized by elemental analysis, NMR spectroscopy,[†] and X-ray crystallography.[‡]

Fig. 1 shows the perspective drawing of the $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+}$ cation with atomic numbering. The four $\mu\text{-dppm}$ ligands are arranged in a saddle-like configuration, with two $\mu\text{-dppm}$ ligands on opposite ends folding up and the other two down. The sulfur atom occupies the apex of a distorted square pyramid, projecting above the Cu_4 plane. The relatively long Cu–Cu bond distances compared to other $d^{10}\text{-}d^{10}$ copper systems are probably a result of the steric requirement of the $\mu_4\text{-sulfur}$ atom.^{7a,e,8} A tetranuclear copper(i) dppm complex, $[\text{Cu}_4(\text{dppm})_4(\text{CS}_3)_2]$ consisting of a square arrangement of copper atoms with the dppm ligands bridging the edges with the same two-up and two-down conformation of the $\mu\text{-dppm}$ ligands, has also been reported.⁹ It is interesting to note the different bonding modes of sulfur in

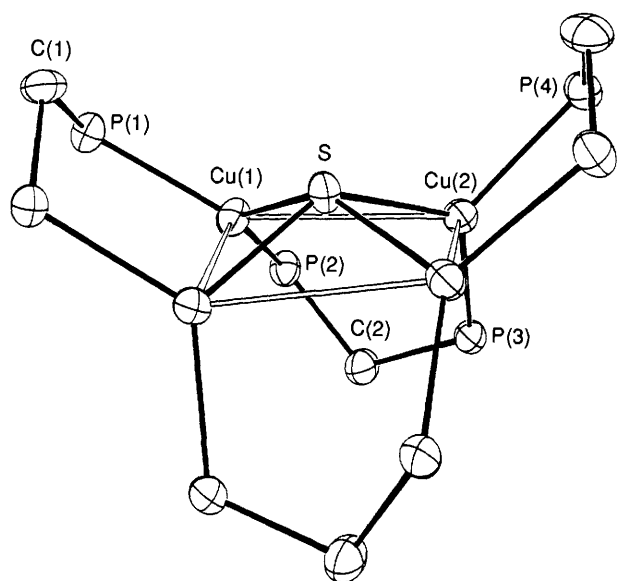


Fig. 1 Perspective drawing of the $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+}$ cation showing the atomic numbering scheme with the phenyl rings omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): Cu(1)–Cu(2) 3.128(1), Cu(1)–Cu(2')^a 2.869(1), Cu(1)–S 2.267(1), Cu(2)–S 2.268(2), Cu(1)–P(1) 2.267(3), Cu(1)–P(2) 2.243(3), Cu(2)–P(3) 2.247(3), Cu(2)–P(4) 2.291(3); Cu(1)–S–Cu(2) 87.19(7), Cu(1)–S–Cu(1')^a 143.2(2), Cu(1)–S–Cu(2')^a 78.49(6), Cu(2)–S–Cu(1')^a 78.45(5), Cu(2)–S–Cu(2')^a 133.5(2), Cu(1')^a–S–Cu(2')^a 87.18(6), S–Cu(1)–P(1) 109.1(1), S–Cu(1)–P(2) 127.47(9), S–Cu(2)–P(3) 124.9(1), S–Cu(2)–P(4) 109.4(2), P(1)–Cu(1)–P(2) 121.28(9), P(3)–Cu(2)–P(4) 125.6(1) (^a symmetry code: 1 – x, y, ½ – z).

[†] Satisfactory elemental analysis; IR, cm^{-1} (Nujol mull) 839 [v(P–F)]; ¹H NMR (CD_2Cl_2 ; Me_4Si) δ 3.20 (br s, 8 H, CH_2), 7.04–7.33 (m, 80 H, Ph); ³¹P NMR ($[\text{H}_2\text{O}]_2\text{Me}_2\text{CO}$; H_3PO_4) δ –11.81.

[‡] *Crystal data*: $[\text{Cu}_4\text{C}_{100}\text{H}_{88}\text{P}_8\text{S}]2\text{PF}_6 \cdot 2\text{Me}_2\text{CO}$, $M = 2229.90$, monoclinic, space group $C2/c$, crystal dimensions $0.11 \times 0.14 \times 0.21$ mm, $a = 27.883(5)$, $b = 16.513(2)$, $c = 24.008(3)$ Å, $\beta = 109.33(1)^\circ$, $V = 10431(8)$ Å³, $Z = 4$, $D_c = 1.420$ g cm^{-3} , $D_m = 1.42$ g cm^{-3} , μ (Mo–K α) = 10.45 cm^{-1} , $F(000) = 4568$, no. of parameters 551, $R = 0.074$, $R_w = 0.090$ for 5042 observed data with $|F_o| > 3\sigma|F_o|$ [$R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, with $w = 4F_o^2/[\sigma^2(F_o^2) + (0.40F_o^2)^2]$]. $S = [\sum w(|F_o| - |F_c|)^2/(m - p)]^{1/2}$. Diffraction data were collected on an Enraf–Nonius diffractometer with graphite monochromated Mo–K α radiation ($\lambda = 0.71073$ Å). The structure was solved by the heavy-atom method and refined by full-matrix least-squares analysis. All calculations were performed on a MicroVax II computer using the Enraf–Nonius SDP package (ref. Enraf–Nonius Structure Determination Package, SDP, Enraf–Nonius, Delft, 1985). Atomic coordinates, thermal parameters, bond distances and angles have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.

the CS_3^{2-} anions of $[\text{Cu}_4(\text{dppm})_4(\text{CS}_3)_2]$ and the $\mu_4\text{-S}$ of $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+}$. In $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-S})]^{2+}$, the Cu(1)–S–Cu(2) and Cu(1')–S–Cu(2') angles of 87.19(7) $^\circ$ and 87.18(6) $^\circ$ are larger than those for Cu(1)–S–Cu(2') [78.49(6) $^\circ$] and Cu(2)–S–Cu(1') [78.45(5) $^\circ$]. The smaller Cu–S–Cu angles for the latter probably arise from the folding up of the $\mu\text{-dppm}$ units attached to the copper atoms toward the sulfur apex. The presence of two acetone molecules as solvent of crystallization has also been supported by the observation of methyl resonance signal in the ¹H NMR spectrum of a freshly prepared sample (before loss of solvent) at $\delta(\text{CD}_2\text{Cl}_2; \text{Me}_4\text{Si})$ 2.1 (s, 12 H), characteristic of acetone.

The electronic absorption spectrum of $[\text{Cu}_4(\text{dppm})_4(\mu_4\text{-S})](\text{PF}_6)_2$ in MeCN shows low energy absorption in the 330–400 nm region (Fig. 2). Excitation of $[\text{Cu}_4(\text{dppm})_4(\mu_4\text{-S})](\text{PF}_6)_2$ at $\lambda > 350$ nm both in the solid-state and in fluid solutions resulted in intense long-lived yellow-orange emission (Fig. 3). The photophysical data are summarized in Table 1. The long excited-state lifetime observed suggests that the emission is most likely associated with a spin-forbidden transition. We suggest that with the good σ -donating capability of the sulfide ion, the low energy emitting state should bear a large amount of ligand-to-metal charge transfer [LMCT ($\text{S}^{2-} \rightarrow \text{Cu}_4$)] character, mixed into the metal-centred $3d^9 4s^1$ state of Cu^{I} which has been modified by copper–copper interaction in the tetramer. Similar findings have been observed in other $d^{10}\text{-}d^{10}$ systems.⁷ The phosphorescent state of $[\text{Cu}_4(\text{dppm})_4(\mu_4\text{-S})]^{2+*}$ is found to be quenched by pyridinium acceptors via an outersphere electron transfer process. The bimolecular quenching rate constants are tabulated in Table 2. An excited-state reduction potential [$E^0(\{\text{Cu}_4\text{S}\}^{3+}/\{\text{Cu}_4\text{S}\}^{2+*})$] of –1.72(1) V (vs. SCE) has been estimated through oxidative quenching studies with the series of

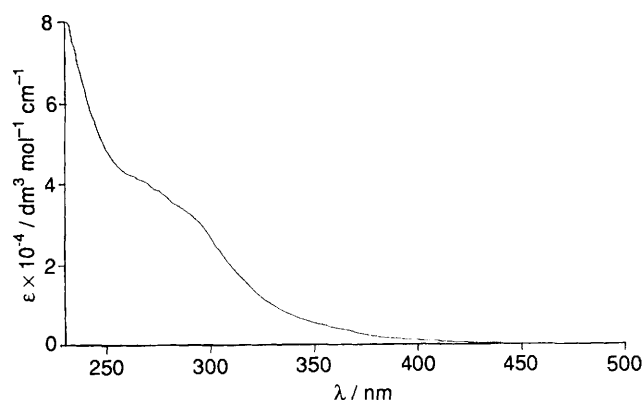


Fig. 2 Electronic absorption spectrum of $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-S})](\text{PF}_6)_2$ in MeCN at 298 K

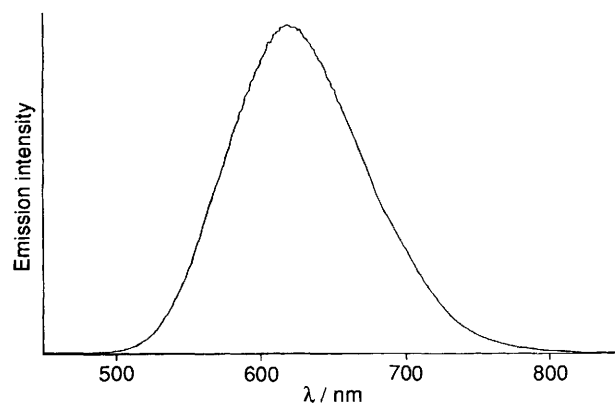


Fig. 3 Emission spectrum of $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-S})](\text{PF}_6)_2$ in degassed MeCN at 298 K

Table 1 Photophysical data for $[\text{Cu}_4(\mu\text{-dppm})_4(\mu_4\text{-S})](\text{PF}_6)_2$

Absorption $\lambda_{\text{max}}/\text{nm}$ ($\epsilon_{\text{max}}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	Emission		
	Medium (T/K)	$\lambda_{\text{em}}/\text{nm}$	$\tau_0/\mu\text{s}$
265 (41 490), 285sh (34 650) ^a	Solid (298)	579	3.6 ± 0.1
	Solid (77)	606	
	MeCN (298)	618	7.8 ± 0.2 ^b
	Me ₂ CO (298)	622	8.1 ± 0.2 ^b
	PrCN glass (77)	539, 610sh	

^a In MeCN at 298 K. ^b $[\text{Cu}_4] \approx 2 \times 10^{-5} \text{ mol dm}^{-3}$.

pyridinium acceptors, indicative of its strong reducing power in the excited state. The present work represents an interesting class of novel luminescent materials, which are isoelectronic to the $[(\mu_4\text{-P})(\text{AuL})_4]^+$ and $[(\mu_4\text{-As})(\text{AuL})_4]^+$ clusters.¹⁰ Preliminary work shows that $[\text{Cu}_4(\text{dppm})_4(\mu_4\text{-S})](\text{Pt}_6)_2$ reacts thermally with electrophiles such as organic halides. Work is in progress to investigate the photophysical and chemical behaviour of a series of related tetranuclear clusters of copper, silver and gold.

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Table 2 Rate constants for the quenching of $[\text{Cu}_4(\text{dppm})_4(\mu_4\text{-S})]^{2+*}$ by pyridinium acceptors in degassed MeCN (0.1 mol dm⁻³ Bu₄NPF₆)

Quencher ^a	$E(\text{A}^{+/0})/\text{V}$ (vs. SCE)	$k_q/\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
4-cyano- <i>N</i> -methylpyridinium	-0.67	5.50×10^9
4-methoxycarbonyl- <i>N</i> -methylpyridinium	-0.78	3.35×10^9
4-aminoformyl- <i>N</i> -ethylpyridinium	-0.93	1.77×10^9
3-aminoformyl- <i>N</i> -methylpyridinium	-1.14	1.84×10^8
<i>N</i> -ethylpyridinium	-1.36	5.59×10^6
4-methyl- <i>N</i> -methylpyridinium	-1.49	1.50×10^6

^aAll the compounds are hexafluorophosphate salts.

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