

Luminescent Three-co-ordinated Dinuclear Copper(I) Complexes of Bis(diphenylphosphino)methane: Photophysical Properties and Crystal Structure

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Reaction between $[\text{Cu}_2(\mu\text{-dppm})_2(\text{MeCN})_4]^{2+}$ [dppm = bis(diphenylphosphino)methane] and substituted pyridines or triphenylphosphine (L) in dichloromethane gave products $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}_2]^{2+}$ which possess long-lived emissive electronic excited states in fluid solution at room temperature.

The study of the photoluminescent properties of d^{10} metal complexes has been receiving current attention.¹⁻⁹ A number of polynuclear complexes of $\text{Au}^{1,2a,b,d,f,5c,6,8}$, $\text{Ag}^{1,2c,d}$ and $\text{Cu}^{1,2e}$ containing bridging phosphine ligands have been reported which show intriguing photophysical and photochemical properties. We have also investigated the spectroscopic properties of $[\text{Cu}_2(\mu\text{-dppm})_2(\text{MeCN})_4][\text{ClO}_4]_2$ [dppm = bis(diphenylphosphino)methane]^{2g} which has also been found to be emissive in fluid solutions. Herein is described the synthesis and spectroscopic properties of complexes $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}_2][\text{ClO}_4]_2$ [L = PPh_3 , pyridine (py), or 4-substituted pyridines X-py, where X = 4- $\text{ClC}_6\text{H}_4\text{CH}=\text{CH}$ (L^1), 4- $\text{O}_2\text{NC}_6\text{H}_4\text{CH}_2$ (L^2), $\text{PhCH}=\text{CH}$ (L^3) or Me (L^4)] and the crystal structure of the complex with L^1 . We have found that the co-ordinated acetonitrile in $[\text{Cu}_2(\mu\text{-dppm})_2(\text{MeCN})_4][\text{ClO}_4]_2$ is substitutionally labile and is easily replaced by nitrogen bases. This work provides a new entry to donor-acceptor supramolecules based on the $[\text{Cu}_2(\mu\text{-dppm})_2(\text{py})_2]^{2+}$ luminophore.

The precursor complex $[\text{Cu}_2(\mu\text{-dppm})_2(\text{MeCN})_4][\text{ClO}_4]_2$ was prepared by the literature method.¹⁰ Treatment of $[\text{Cu}_2(\mu\text{-dppm})_2(\text{MeCN})_4][\text{ClO}_4]_2$ (0.1 g) with an excess of ligand L (0.1 g) in dichloromethane (30 cm^3) at room temperature for 15 min afforded the crystalline complexes $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}_2][\text{ClO}_4]_2$ in high yield (> 70%) upon precipitation with diethyl ether. The complexes were recrystallised by diffusion of diethyl ether into acetone solutions. These species have been characterised by X-ray crystallography,¹¹ \dagger and elemental analyses.

Fig. 1 shows a perspective view of the cation in $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}_2][\text{ClO}_4]_2$ **1**. The co-ordination geometry around each copper atom is trigonal planar with bonding to two P and one N atom. The two copper atoms are doubly bridged by two dppm ligands and the two nitrogen ligands are co-ordinated to separate metal atoms at opposite ends of the structure. In contrast to $[\text{Au}(\text{dppm})_2]^{2+}$ ^{2a,b,6} in which a metal-metal

interaction is present, the Cu...Cu separation in **1** is greater than 3.7 Å indicating the absence of such an interaction. The Cu-N bond lengths, 2.063(7) and 2.072(7) Å, are practically identical to those found in $[\text{Cu}_2(\mu\text{-dppm})_2(\text{MeCN})_4][\text{ClO}_4]_2$.¹⁰ The co-ordinated ligand L^1 does not adopt a planar configuration.

The spectroscopic data for the copper complexes are summarized in Table 1. Fig. 2 shows the electronic absorption and emission spectra of $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}_2][\text{ClO}_4]_2$ **1**, $[\text{Cu}_2(\mu\text{-dppm})_2(\text{py})_2][\text{ClO}_4]_2$ **2** and $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}_2][\text{ClO}_4]_2$ **3** in dichloromethane at room temperature. The absorption spectra of **2** and **3** exhibit a broad shoulder absorption between 300 and 350 nm with $\epsilon_{\text{max}} \approx 1 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, which is similar to that of $[\text{Cu}_2(\mu\text{-dppm})_2(\text{MeCN})_4][\text{ClO}_4]_2$ and probably arises from a metal-perturbed intraligand $\pi \rightarrow \pi^*$ transition of co-ordinated phosphine. The absorption spectrum of **1** is dominated by a more intense absorption band at λ_{max} 315 nm ($\epsilon_{\text{max}} = 4.19 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). Since this band is also found in the absorption spectrum of the free ligand, L^1 , this is assigned to the intraligand $\pi \rightarrow \pi^*$ transition of L^1 .

The complexes exhibit photoluminescence both in the solid state or in fluid solution (CH_2Cl_2) at room temperature. Excitation in the range 300–360 nm of degassed dichloromethane solutions of the complexes gives emission at ca. 520 nm. The free ligand dppm also displays emission at 500 nm in dichloromethane upon excitation in the range 300–350 nm. The emission maximum at 520 nm of the complexes is considerably red shifted from that of dppm. A similar red shift in energy was also found in $[\text{Cu}(\text{dppe})(\text{BH}_4)]$ [dppe = 1,2-bis(diphenylphosphino)ethane] (537 nm emission vs. the 500 nm emission of free dppe) by Kutal and co-workers.⁹ In the emission spectrum of **1** a weak high-energy peak appears at 450 nm. An intraligand $\pi \rightarrow \pi^*$ state is suggested as an analogous band is observed in the emission spectrum of free L^1 . The photophysical properties of the complexes $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}_2][\text{ClO}_4]_2$ are summarized in Table 1. Life-times were obtained by single-exponential decay fitting. It is interesting that the emission lifetime (0.4 μs) of $[\text{Cu}_2(\mu\text{-dppm})_2(\text{MeCN})_4][\text{ClO}_4]_2$ is significantly shorter than the values ($\geq 24 \mu\text{s}$) of related complexes containing nitrogen bases or PPh_3 as axial ligands. It has been reported¹⁰ that the acetonitrile ligands in $[\text{Cu}_2(\mu\text{-dppm})_2(\text{MeCN})_4][\text{ClO}_4]_2$ are in a fast dissociation equilibrium in fluid solution. This fast on-off co-ordination is not likely to occur for better donor ligands, such as pyridine or triphenylphosphine, leading to longer emission lifetimes.

The co-ordination of pyridine and its substituted derivatives or triphenylphosphine to $[\text{Cu}_2(\mu\text{-dppm})_2]^{2+}$ results in the formation of dinuclear complexes having extraordinarily long-lived excited states. Since the structure of the auxiliary nitrogen base or phosphine is easily tunable, this work may provide an

\dagger Crystal data for $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}_2][\text{ClO}_4]_2$ **1**: $\text{C}_{76}\text{H}_{64}\text{Cl}_4\text{Cu}_2\text{N}_2\text{O}_8\text{P}_4$, $M = 1526.2$, triclinic space group $P\bar{1}$ (no. 2), $a = 10.421(4)$, $b = 17.745(6)$, $c = 20.014(8)$ Å, $\alpha = 93.03(3)$, $\beta = 99.95(3)$, $\gamma = 98.52(3)^\circ$, $U = 3593$ Å³, $Z = 2$, $D_c = 1.441 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 8.85 \text{ cm}^{-1}$, $F(000) = 1568$, no. of variables 455, no. of unique data measured 6650, no. of observed data with $|F_o| \geq 3\sigma|F_o|$ 5075, $R(\Sigma|F_o| - |F_c|/\Sigma|F_o|) = 0.069$, $R^2(\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2) = 0.091$. Weighting scheme $w = 4F_o^2/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$. The residual extrema in the final difference map were 0.69 and -0.51 e \AA^{-3} . Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo-K α radiation (0.710 73 Å) at room temperature (298 K). The structure was solved by a combination of Patterson and direct methods. Refinement was by full-matrix least squares. A perchlorate ion was found to be highly disordered. All computations were performed on a MicroVax II computer using Enraf-Nonius SDP programs.¹² Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii-xxviii.

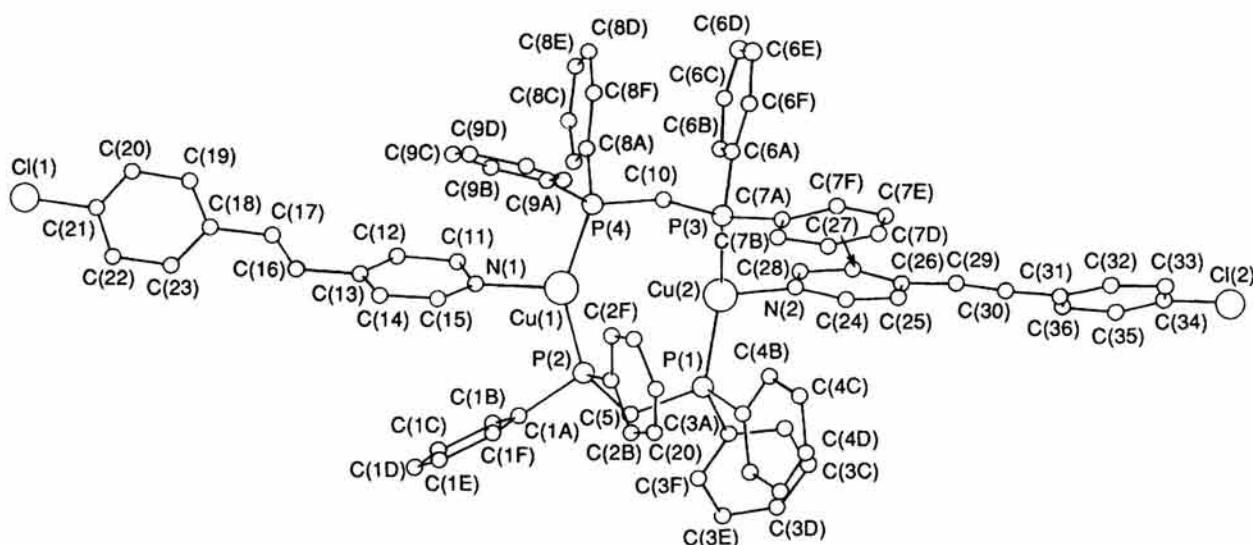


Fig. 1 A perspective view of the $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}^{1.2}]^{2+}$ cation. Selected bond lengths (Å) and angles ($^\circ$): Cu(1)–N(1) 2.063(7), Cu(1)–P(2) 2.237(3), Cu(1)–P(4) 2.229(2), Cu(2)–N(2) 2.072(7), Cu(2)–P(1) 2.272(2), Cu(2)–P(3) 2.275(2), P(2)–Cu(1)–P(4) 131.7(2), P(2)–Cu(1)–N(1) 110.2(2), P(4)–Cu(1)–N(1) 108.7(2), P(1)–Cu(2)–P(3) 137.0(1), P(1)–Cu(2)–N(2) 108.5(2), P(2)–Cu(2)–N(2) 101.4(2)

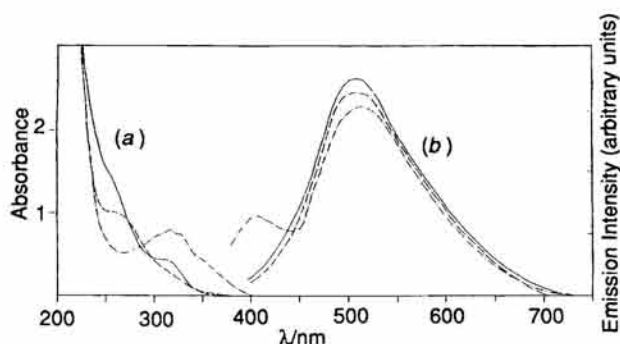


Fig. 2 UV/VIS absorption (a) and emission spectra (b) of $[\text{Cu}_2(\mu\text{-dppm})_2(\text{py})_2][\text{ClO}_4]_2$ **2** (—), $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}^2][\text{ClO}_4]_2$ **3** (---) and $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}^{1.2}][\text{ClO}_4]_2$ **1** (-·-·-)

Table 1 Photophysical properties of complexes $[\text{Cu}_2(\mu\text{-dppm})_2\text{L}_2][\text{ClO}_4]_2$ in dichloromethane at room temperature

L	$\lambda_{\text{abs}}/\text{nm}$	$\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	$\tau/\mu\text{s}^a$	Φ_{em}^b
MeCN ^c	314	1.12×10^4	530	0.4	1.0×10^{-4}
	255	3.00×10^4	550	75	3.4×10^{-2}
PPh ₃	310 (sh) ^d	4.76×10^3			
	306	8.54×10^3	525	27	1.8×10^{-3}
py	315	4.19×10^4	425	0.2	5.9×10^{-4}
			525	51	
L ¹	255	4.88×10^4	515	24	3.4×10^{-3}
	315 (sh)	1.33×10^4			
L ²	312	4.21×10^4	424	0.2	6.1×10^{-5}
			525	30	
L ⁴	308	9.14×10^3	525	45	1.0×10^{-3}

^a Emission life-time. ^b Emission quantum yield. ^c Four ligands are coordinated to two copper atoms. ^d sh = Shoulder.

entry into a new class of donor–acceptor supramolecules for studies of intramolecular photo-induced energy and electron-transfer reactions.

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