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A highly luminescent tetranuclear copper(I) cluster: structure and photophysical properties

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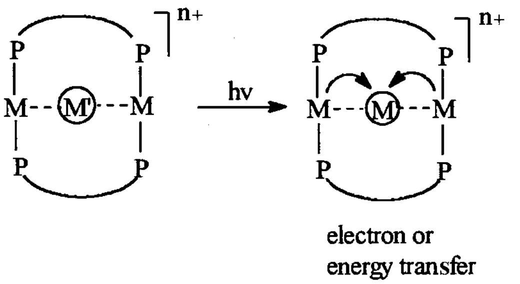
Abstract

A tetranuclear copper(I) cluster $Cu_4(C{\equiv}CPh)_4L_2$ (**1**) [$L = Ph_2PCH_2(CH_2OCH_2)_2CH_2PPh_2$] prepared by self assembly reaction of $[Cu(C{\equiv}CPh)]_n$ with the bridging diphosphine ligand L comprises a $Cu_2(L)_2$ metallomacrocycle with two phenylethynyl copper(I) units encapsulated in the host site. The four Cu(I) are coplanar and arranged as a zigzag chain and the complex displays an intense emission at 522 nm with a lifetime of 9.8 μs and a quantum yield of 0.42 in dichloromethane. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Tetranuclear Cu(I) cluster; Metallomacrocycle; Zigzag chain; Luminesence

1. Introduction

One of our approaches to photocatalysis is to develop new metallomacrocycles with long-lived excited states and which could function as molecular hosts for coordinative unsaturated organometallic species [1]. We anticipate that highly reactive organometallic species can be generated inside the host via light excitation and such species can find applications in host–guest organometallic photochemistry (Scheme 1). Recent studies showed that coordination of bridging long chain diphosphine ligands to d^{10} metal ions provides an entry to new metallomacrocycles ([1]a–b, [2,3]). In some cases studied, the copper(I) complexes display interesting properties as light-emitting species and photocatalysts [4,5]. Herein is described the encapsulation of phenylethynylcopper(I) units using a binuclear copper(I) complex of 1,8-bis(diphenylphosphino)-3,6-dioxaoctane, L. Besides its unique structure, complex **1** is strongly luminescent with a quantum yield even comparable to $[Pt_2(P_2O_5H_2)_4]^{4-}$ [6] ($\phi = 0.53$) and $[Au_2(dppm)_2]^{2+}$ [dppm = bis(diphenylphosphino)methane] [7] ($\phi = 0.20$) in solution at room temperature (r.t.).



Scheme 1. Schematic diagram showing the host–guest photochemistry in metallomacrocycle.

2. Results and discussion

2.1. Preparation and spectroscopic characterization

Reaction of L with stoichiometric amount of phenylethynylcopper(I) in dichloromethane breaks

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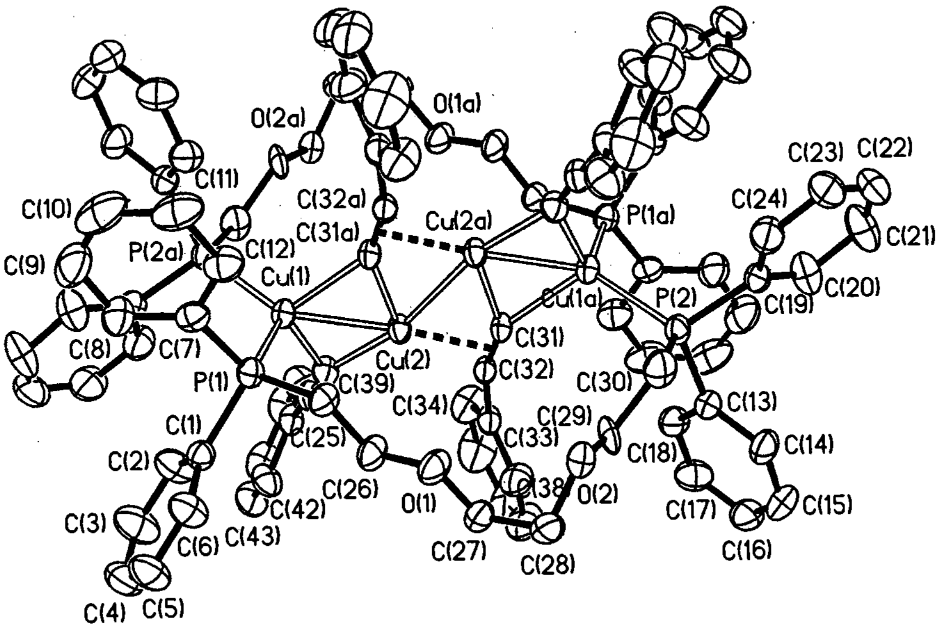

Fig. 1. Perspective drawing of complex **1**. Hydrogen atoms are omitted for clarity.

down the polymeric structure of the latter to afford **1**. Complex **1** is an air-stable, bright yellow crystalline solid, but its solution decomposes upon prolonged standing in air. Its infrared spectrum exhibits two ν(C≡C) (1917 and 2047 cm^{-1}) in contrast to the only one ν(C≡C) stretch at 1933 cm^{-1} for phenylethynylcopper(I). This corresponds to the existence of two types of phenylethynyl groups in **1**.

2.2. Crystal structure

A perspective drawing of **1** is shown in Fig. 1 and a diagram showing its core structure is depicted in Fig. 2. Selected bond distances and relevant bond angles are listed in Table 1. Complex **1** can be viewed as a metallomacrocycle $[Cu_2(L)_2]^{2+}$ encapsulated with two $Cu(C{\equiv}CPh)_2$ fragments. The core structure of **1** closely resembles to $[Cu_4(C{\equiv}CPh)_4(PMe_3)_4]$ [8] in that the Cu_4 unit also has a zigzag geometry. The four copper atoms are coplanar as a consequence of the centrosymmetry. The terminal Cu(1) atoms are best described as distorted tetrahedral while the inner Cu(2) atoms are trigonally bound to three phenylethynyl groups via two σ-bonding and one side-on π-bonding mode. The C(39)–C(40) distance of 1.200(5) Å and the C(39)–C(40)–C(41) angle of 176.5(4)° are typical to those found for a terminal C≡C triple-bond. However, the relatively long C≡C distance [C(31)–C(32) of 1.225(4)

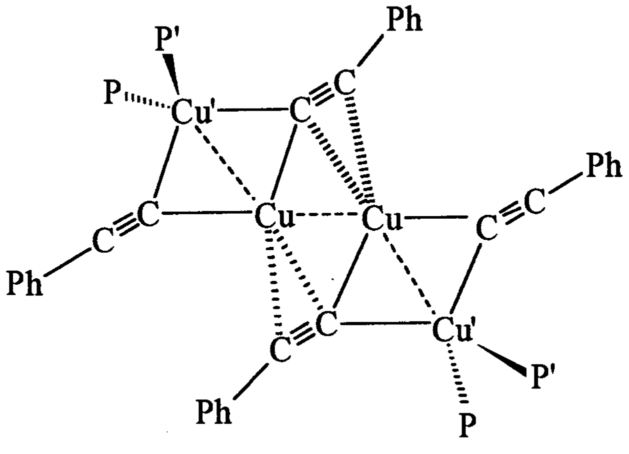

Fig. 2. Diagram showing the core structure of complex **1**.

Table 1
Selected bond lengths (Å) and bond angles (°) of complex **1**

Cu(1)–Cu(2)	2.409(1)	Cu(1a)–C(31)	2.147(3)
Cu(2)–Cu(2A)	2.564(1)	Cu(2a)–C(31)	2.045(3)
Cu(1)–C(31a)	2.147(3)	Cu(1)–P(1)	2.269(1)
Cu(2)–C(31a)	2.045(3)	Cu(1)–P(2a)	2.261(1)
Cu(1)–C(39)	2.138(3)	C(31)–C(32)	1.225(4)
Cu(2)–C(39)	1.970(4)	C(39)–C(40)	1.200(5)
Cu(2)–Cu(1)–P(1)	114.3(1)	Cu(2)–Cu(1)–P(2a)	129.6(1)
P(1)–Cu(1)–C(39)	118.8(1)	C(39)–Cu(1)–P(2a)	101.7(1)
P(1)–Cu(1)–P(2a)	116.1(1)	P(1)–Cu(1)–C(31a)	100.7(1)
Cu(2)–Cu(1)–C(31a)	53.0(1)	P(2a)–Cu(1)–C(31a)	116.6(1)
C(39)–Cu(1)–C(31a)	102.9(1)	Cu(1)–Cu(2)–C(32)	163.2(1)
Cu(1)–Cu(2)–C(31)	157.7(1)	Cu(1)–Cu(2)–C(39)	57.4(1)
C(31)–Cu(2)–C(32)	34.3(1)	C(32)–Cu(2)–C(39)	109.3(1)
C(31)–Cu(2)–C(39)	143.6(1)	C(31)–Cu(2)–Cu(2a)	50.9(1)
Cu(1)–Cu(2)–Cu(2a)	108.5(1)	C(39)–Cu(2)–Cu(2a)	165.4(1)
C(32)–Cu(2)–Cu(2a)	85.2(1)	C(31)–Cu(2)–C(31a)	103.3(1)
Cu(1)–Cu(2)–C(31a)	56.9(1)	C(39)–Cu(2)–C(31a)	113.1(1)
C(32)–Cu(2)–C(31a)	137.6(1)	C(39)–C(40)–C(41)	176.5(4)
Cu(2a)–Cu(2)–C(31a)	52.3(1)	C(31)–C(32)–C(33)	160.7(4)
Cu(2)–Cu(1)–C(39)0	50.9(1)		

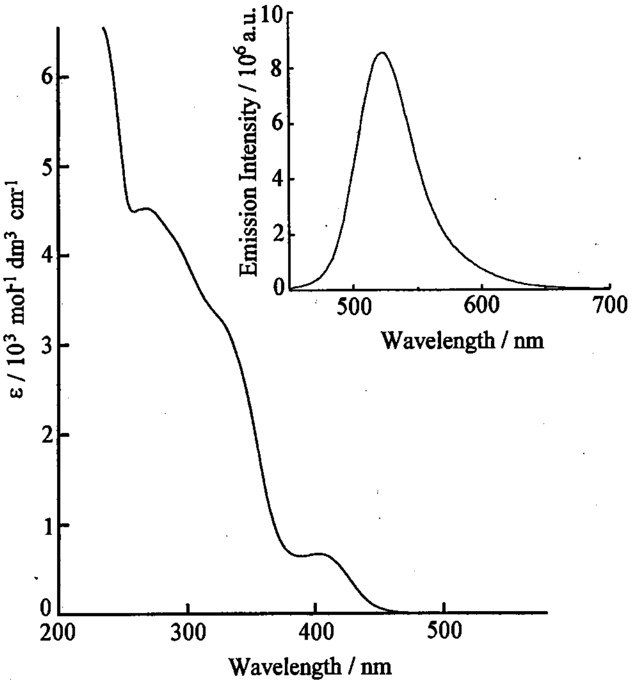

Fig. 3. UV–vis absorption spectrum of complex **1** in dichloromethane. The insert graph shows its emission spectrum in dichloromethane at r.t.

Å] and deviation of C(31)–C(32)–C(33) angle from linearity [160.7(4)°] are suggestive of a side-on bonding between the C≡C moiety and Cu^{I} centre. Thus two of the four ethynyl groups are both 2e–3c (two-electron three-centered) bonded and π-bonded. The differences in Cu(1)–C(31a)/Cu(1)–C(39) and Cu(2)–C(31a)/Cu(2)–C(39) distances suggest the phenylethynyl bridge to be asymmetric. Two distinct Cu–Cu distances are present in the complex, of which the shorter distance belongs to the Cu atom pair bridged by a phenylethynyl group and the longer one belongs to an unbridged Cu atom pair. The Cu(1)–Cu(2) distance [2.409(1) Å] is shorter than the separation found in metallic copper (2.56 Å), and is indicative of weak Cu(I)–Cu(I) interaction. The Cu(2)–Cu(2a) distance [2.564(1) Å] is much longer suggesting that there could be no interaction between Cu(2) and Cu(2a) atom. Thus it is likely that the two $Cu_2(C{\equiv}CPh)_2$ cores are held together by the Cu(I)-phenylethynyl π-bonding interaction.

2.3. Photophysical properties

As shown in Fig. 3, the electronic absorption spectrum of **1** in dichloromethane is characterized by an intense absorption band at ca. 270 nm ($\varepsilon = 45240$ dm^3 mol^{-1} cm^{-1}) with a shoulder at ca. 320 nm ($\varepsilon = 33650$ dm^3 mol^{-1} cm^{-1}) and a weaker absorption band at ca. 408 nm ($\varepsilon = 7770$ dm^3 mol^{-1} cm^{-1}). The absorptions at 270 nm and 320 nm are not uncommon in copper(I)-phenylethynyl complexes containing phosphine ligands ([4]a) and are due to the intraligand and/or Cu(I) → phosphine charge transfer transition. The 408 nm band deserves attention since it has a high ε_{max} and similar absorption band has not been reported in the related $[Cu_3(dppm)_3(\mu^3\text{-}\eta^1\text{-}C{\equiv}CR)_n]^+$ ($n = 1$, 2) ([9]a) and $[Cu_4(PPh_3)_4(\mu^3\text{-}\eta^1,\eta^1,\eta^2\text{-}C{\equiv}CC_6H_4OMe\text{-}p)_3]^+$ ([9]b) complexes. We attribute it to come from the $Cu_4(C{\equiv}CPh)_4$ core and a tentative assignment is admixture of the metal cluster 3s/ 3d → 4p modified by Cu(I) → π^*(C≡CPh).

Excitation of solid or fluid solutions of **1** at 300–400 nm gives an intense emission, the photophysical data of which are summarized in Table 2. At r.t., the solid state emission shows a maximum at 533 nm with a weak band at 575 nm. Upon cooling to 77K, the emission maximum blue shifts to 523 nm which is similar to that recorded in fluid solutions at r.t. and the lower energy emission at 575 nm becomes a weak shoulder (See insert in Fig. 2). Interestingly, the emission has a long lifetime and a high quantum yield in non-coordinating solvent. The measured quantum yield of 0.42 in CH_2Cl_2 is the highest compared to the related literature values for luminescent copper(I) complexes ([4]a). In fact, it is even comparable to that of 0.53 reported for $[Pt_2(P_2O_5H_2)_4]^{4-}$ [6]. We suggest that the emission comes from the excited state of the $Cu_4(C{\equiv}CPh)_4$ core. As it is wrapped by the two bridging diphosphine ligands, this would disfavor the solvent induced non-radiative decay pathways which has commonly been observed for copper(I) photoluminescence and account for the high emission quantum yield.

3. Conclusion

We find that encapsulation of two Cu(C≡CPh) units into the $[Cu_2(L)_2]^{2+}$ metallomacrocycle gives a Cu_4 cluster with interesting spectroscopic properties. The observation of a high emission quantum yield for $Cu_4(C{\equiv}CPh)_4L_2$ is intriguing and suggests the potential applications of luminescent copper(I) compounds as light emitting diode materials. We anticipate a systematic variation of the bridging diphosphine ligand can lead to a family of metallomacrocycles for development of novel organocopper(I) complexes.

Table 2
Photophysical data for complex **1** measured at r.t.

Solvent	λmax (nm)	t (μs)	Quantum yield
CH_2Cl_2	522	9.8	0.42
MeCN	522	4.4	0.23
MeOH	521	3.9	0.20
Solid (r.t.)	533	6.7	–
Solid (77 K)	523	5.9	–

4. Experimental

4.1. General data

All reactions were performed under a nitrogen atmosphere with the use of standard Schlenk techniques. The solvents were purified by standard methods. The compounds $[Cu(C\equiv CPh)]_n$ and L were prepared as described in literature [10,11]. IR spectra were recorded on a Nicolet 20SXC FT-IR spectrometer as nujol mulls. The ^{31}P-NMR spectra were recorded on a JEOL GSX-270 spectrometer and $CDCl_3$ as solvent. Elemental analyses of C and H were carried out by Butterworth Laboratories. UV–vis spectra were recorded on a Perkin Elmer spectrophotometer Lambda 19. Emission spectra were obtained on a Spex Fluorolog-2 spectrophotometer and emission lifetimes of the complexes, in both solid-state and solution, were measured with a Quanta Ray DCR-3 Nd-YAG laser.

4.2. Preparation of complex **1**

To a dichloromethane (25 ml) solution of L (0.243 g, 0.5 mmol) was added $[Cu(C\equiv CPh)]_n$ (0.164 g, 1 mmol) and the mixture was stirred at r.t. for 4 h. The yellow suspension was filtered to obtain a yellow solution which was concentrated and recrystallised from CH_2Cl_2–MeOH solution to afford yellow prisms of **1**. Yield: 0.55 g (50%). Found (%): C, 67.67; H, 5.17; Anal. Calc. (%) for $C_{92}H_{84}Cu_4O_4P_4$: C, 67.72; H, 5.19. IR (Nujol) $\nu(C\equiv C)$ cm^{-1}, 1917w, 2046.8m. ^{31}P-NMR ($CDCl_3$), δ/ppm -12.2, -17.1.

4.3. X-ray data collection and structure refinement

Suitable yellow crystals of **1** were obtained by slow diffusion of methanol into its dichloromethane solution.

Crystal data. $C_{92}H_{84}Cu_4O_4P_4$; $M = 1631.6$; monoclinic, space group $P2_1/n$; $a = 14.980(1)$; $b = 14.359(1)$, $c = 18.545(1)$ Å; $\beta = 91.61(1)°$; $V = 3987(2)$ Å^3; $Z = 2$, $D_{calc} = 1.359$ g cm^{-3}, $\mu(Mo{-}K_\alpha) = 1.184$ mm^{-1}, $F(000) = 1688$.

A crystal of dimension $0.16 \times 0.20 \times 0.40$ mm^3 was mounted on a glass fibre. Intensity data were collected on a Rigaku RAXIS IIc image plate diffractometer using graphite monochromatic Mo–K_α radiation ($\lambda = 0.71073$ Å) [12]. The measurement was carried out by ω-2θ scan technique at 294 K and in the range $3 \leq \theta \leq 55°$; $0 \leq h \leq 18$, $-18 \leq k \leq 18$, $-23 \leq l \leq 23$. Absorption correction was based on ABSCOR [13] (minimum and maximum transmission factors 0.947, 1.012). Upon averaging 12332 reflections, 7491 of which were uniquely measured, 5989 with $F \geq 6\sigma(F)$ were considered to be observed and used in structural analysis. The structure was solved by direct methods and refinement by full-matrix least-squares using Siemens SHELXTL PLUS system. Convergence for 491 variable parameters by least-squares refinement on F with $w^{-1} = \sigma^2(F)$ for 5989 having $F \geq 6\sigma(F)$ was reached at $R = 0.053$ and $wR = 0.039$ with goodness of fit of 2.55 $(\Delta/\sigma)_{max} = 0.001$. The final Fourier-difference map was featureless, with maximum positive and negative peaks of 0.40 and -0.42 e Å^{-3}, respectively. O(2) and C(29) are disordered to give the conformations with site occupancy 0.5959 and 0.4041, respectively.

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