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# The Coordination- and Photochemistry of a New Dinuclear Copper(I) Bis(diphenylphosphino)methane (1 : 2) Complex

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**Abstract**—In our attempts to identify new species in the preparation of copper(I)-Dppm (Dppm = bis(diphenylphosphino)methane) complexes under the condition of excess Dppm, we isolated and analyzed a new binuclear copper(I)-Dppm complex, namely, $[(\mu_2\text{-}\eta^1,\eta^1\text{-Dppm})_2Cu_2(\eta^1\text{-Dppm})_2(\mu_2\text{-Cl})](BF_4)$ (**I**). We report here the synthesis, crystal structure (CIF file CCDC no. 1912269), characterizations by various spectroscopic (IR, $^1$HNMR, UV–Vis, powder XRD) techniques and the thermal and luminescent properties of this complex. Its X-ray crystal structure reveals a discrete cationic binuclear copper(I)-Dppm (1 : 2) species for the first time. The binuclear copper centres are bridged by a pair of *cis*-Dppm molecules and one chloride ion, and further consolidated by two *trans*-Dppm molecules in mono-dentate fashion. It exhibits cyan photoluminescence in the solid state at room temperature. This work not only addresses the concern of structural information of binuclear copper(I)-Dppm (1 : 2) complex, but also provides a new way to incorporate sterically hindered ligands into the $\{Cu(\mu_2\text{-}\eta^1,\eta^1\text{-}\textit{trans}\text{-Dppm})_2Cu\}$ scaffold for novel luminous properties.

*Keywords:* copper(I) complexes, bis(diphenylphosphino)methane, luminescence, crystal structure

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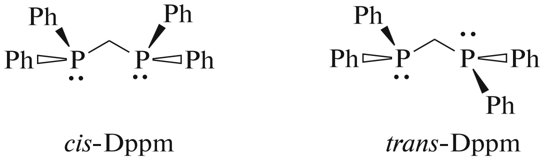
## INTRODUCTION

Copper(I) phosphine complexes has captured the interest of researchers in the organic optoelectronic field for their structural diversity, easily preparation, ability to absorb light in the visible region, intense luminescence, as well as low cost [1–4]. Although tens and hundreds of those complexes have been structurally characterized and widely studied in the literature [3, 5], they are far from completely revealed.

Among them, the copper(I) bis(diphenylphosphino)methane (Dppm) complexes play a very important role in this field [6]. This is closely associated with the geometry configuration (Scheme1) and properties of Dppm [7].



*cis*-Dppm *trans*-Dppm

**Scheme 1.**

It can bind strongly to copper in low oxidation states, has a greater tendency to act either as a monodentate ligand or as a bridging bidentate ligand, can lock together two metal atoms in close proximity and hence promote organometallic reactions involving two metal centres [8]. The mononuclear complexes of the type $[Cu(Dppm)(P^\wedge P)]^+$ ($P^\wedge P$ = Dppm, bis[2-(diphenylphosphino)phenyl] ether: POP) [4] or $[Cu(Dppm)(N^\wedge N)]^+$ ($N^\wedge N$ = bis(imine)) [9] were studied for their potential candidates as cheap emitting materials for electroluminescent devices. Binuclear copper(I)-Dppm complexes $[Cu(\mu_2\text{-}\eta^1,\eta^1\text{-Dppm})_2Cu]^{2+}$ with the metal to ligand ratio 1 : 1 represent the most common complexes [9] in this area and have been widely studied for so many years [9–15]. Rare examples of binuclear copper(I) complexes with different copper to phosphine ligand ratios have also been reported in literature, e.g. one 2 : 1 complex like two 1 : 1.5 complexes like $[WS_4Cu_2(\mu_2\text{-}\eta^1,\eta^1Dppm)(\eta^1\text{-Dppm})_2]$ [16] and $[Cu_2(\text{8-mercaptotheophylline})_2(\mu_2\text{-}\eta^1,\eta^1Dppm)(\eta^1\text{-Dppm})_2]$ [17]. The binuclear Cu(I) systems could act as a convenient source of preorganized dimetal building blocks and were drawing great attention for their photophysical properties [18, 19] and prospective usage as catalysts [21] and sensors for various organic bases [12] or anions [22]. A series of trinuclear copper(I)-Dppm complexes with the copper to ligand ratio 1 : 1 have been reported, including the monocapped complexes, $[Cu_3(\mu_2\text{-}\eta^1,\eta^1Dppm)_3(\mu_3\text{-}X)]^{2+}$, X = C≡CR [23], OH [24] and the bicapped complexes $[Cu_3(\mu_2\text{-}\eta^1,\eta^1Dppm)_3XY]^+$, X ≠ Y = C≡CR, N≡CR or H, OH, Cl, Br, I, CNO et al. [13, 14, 16–18, 25]. Other examples of trinuclear copper(I)-Dppm complexes, including heterometallic complexes like $[MS_4Cu_3(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_3]^+$ [M = Mo [27] or W [16, 28] $[(n\text{-}Bu)_4N][WS_4Cu_3Br_2(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_2]$ [16, 28], as well as $[(Ph)_4P][(\eta^5\text{-}C_5Me_5)WS_3Cu_3Br_3(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)]$ [29] have also been structurally revealed and studied for nonlinear optical material (NLOM). Structurally, the tetranuclear copper(I)-Dppm complexes or clusters are more diverse than the trinuclear ones, typically examples including 'saddle-like' complexes $[Cu_4(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_4(\mu_4\text{-}X)]^{2+}$ (X = S, Se, Te, PPh, C≡C, $WSe_4$, $MoS_4$, $WS_4$) [16, 30], 'step' structures $[(CuX)_4(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_2]$ (X = Cl, Br, I) [31, 32], dimeric structures $[(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_2Cu_2(L\text{-}L)Cu_2(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_2]^{2+}$ (L-L = $O_2CC_6H_4CO_2$ and $O_2CC_2F_4CO_2$ [33, 34], pyridine-2,6-dicarboxylic acid [10], functionalized 2,2'-bipyridyl tetrazole ligands [35], $CN^-$ [19], $[Cu_4(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_4(\mu\text{-}N—N)_3]^{4+}$ (N—N = $NC–(CH_2)_x–CN$ [36], cyano-capped π-conjugated systems [37], metallacycles, $[\{Cu_2(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_2\}(\mu\text{-}(2/3\text{-}PyCO_2))]_2^{2+}$ [38], and other tetranuclear Cu(I) clusters with random structures $[Cu_4(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_2(\mu\text{-}X)_4]$ (X = $SC_5H_{11}$ [39], $PPh_2$ [40]), $S_2P(O^iPr)_2$ [13, 41] $[Cu_4(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_3(\mu_2\text{-}\mu_2\text{-}NS_2)(\mu_2\text{-}\mu_4\text{-}NS_2)]$ [42], $Cu_4(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_4\text{-}[S_2CC(CN)P(O)(OEt)_2]_2$, and $Cu_4(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_3(OPPh_2CH_2PPh_2)[S_2CC(CN)P(O)(OEt)_2]_2$ [43]. High-nuclearity copper(I)-Dppm clusters are countable, including four pentanuclear clusters [42–44], four hexanuclear clusters [13, 45–47], three octanuclear clusters [38, 48], one nonanuclear cluster [43], one decadenuclear clusters [49], etc. It should be noticed that although the fascinating structures and intriguing properties of copper Dppm complexes are extensively studied, the minimum copper to phosphine ligand ratio of all the above copper(I) Dppm complexes is 2 : 3.

Based on the larger steric hindrance of Dppm and the very low coordination numbers of Cu(I), it's big challenge to further reduce the copper to Dppm ratio. Although copper-Dppm complexes are intensively investigated, the complexes with lower copper to Dppm ratios should be revealed in different respect. In this study, we have been prepared a new dinuclearcopper(I)-Dppm (1 : 2) complex, named $[(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_2Cu_2(\eta^1\text{-}Dppm)_2(\mu_2\text{-}Cl)](BF_4)$ (**I**). And we describe herein the synthesis, characterization, thermal and luminescence properties of this complex.

## EXPERIMENTAL

All of the reagents and solvents employed were commercially available and used as received without further purification. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm$^{-1}$ with a WQF-520A FT-IR spectrometer. The electronic absorption spectrum were recorded with a UV-2100 spectrophotometer. The powder X-ray diffraction (PXRD) pattern were recorded with DX-2700 X-ray diffractometer. The TGA curve was recorded on a Q50 Thermogravimetric analyzer (the sample was heated from 20 to 800°C at 10°C/min in the atmosphere of nitrogen). The solid UV–Vis diffuse reflectance spectrum was recorded on a UV-3600 spectrophotometer at room temperature. Emission spectra and lifetime was measured on a Horiba Jobin Yvon Fluoromax-4P-Tcspc spectrometer. The C, H, and N microanalyses were carried out with a CE instruments EA 1110 elemental analyzer.

**Synthesis $[(\mu_2\text{-}\eta^1,\eta^1\text{-}Dppm)_2Cu_2(\mu\text{-}Dppm)_2(\mu_2\text{-}Cl)]\text{-}(BF_4)$ (I).** $Cu(CH_3CN)_4BF_4$ (0.095 g, 0.3 mmol) was dissolved in a methanol solution (6 mL) of bis(diphenylphosphino)methane (0.23 g, 0.6 mmol) under ultrasonication for 5 min, get a white turbid solution, then NaCl (0.0087 g, 0.15 mmol) was added to the turbid solution. After the solution was ultrasonicated for 10 min, the mixture was sealed and heated to 70°C for 20 h. Then cooled to room temperature, the mixture was filtered to give a colorless clear solution. Slow evaporation of the filtrate afforded **I** as colorless crystals after one day. The yield was 39.2% (about 110 mg, based on $Cu(CH_3CN)_4BF_4$).

For $C_{100}H_{88}BF_4P_8ClCu_2$

| | | |
|---|---|---|
| Anal. calcd., % | C, 67.22 | H, 4.96 |
| Found, % | C, 66.83 | H, 4.72 |

FT-IR (KBr; $\nu_{max}$, cm$^{-1}$): 3049 m (CH); 1482, 1435 s (C=C); 1059 v.s ($BF_4^-$). UV–Vis data in $CH_3CN$ ($\lambda_{max}$, nm (ε, L mol$^{-1}$ cm$^{-1}$)): 256 (45500). $^1H$ NMR ($CD_3OH$; 500 MHz; δ, ppm): 3.2 (s., 2H, $Ph_2PCH_2PPh_2$), ~7.1–7.3 (m., 20 H, $Ph_2PCH_2PPh_2$).

**X-ray crystal-structure determination.** An X-ray-quality crystal of complex was grown from methanol at 5°C, and X-ray crystallographic data were recorded by mounting a colorless single-crystal of complex **I** (0.36 × 0.18 × 0.08 mm) onto a glass fiber. Intensity data of title complex was collected on a Bruker SMART APEX CCD diffractometer (Mo$K_\alpha$ source). Absorption corrections were applied by using the program CrysAlis (multi-scan). The structures were solved by direct methods, and non-hydrogen atoms were refined anisotropically by least-squares on $F^2$ using the SHELXTL program [50–52]. The hydrogen atoms of organic ligands were generated geometrically. The crystallographic data for complex **I** are presented

**Table 1.** Crystallographic data and structure refinement summary for complex **I**

| Parameter | Value |
|---|---|
| Chemical formula | $C_{100}H_{88}BF_4P_8ClCu_2$ |
| Formula weight | 1786.80 |
| Crystal system | Triclinic |
| Space group | $P\bar{1}$ |
| $a$, Å | 15.0074(9) |
| $b$, Å | 15.5192(9) |
| $c$, Å | 21.6966(14) |
| α, deg | 82.895(2) |
| β, deg | 70.457(2) |
| γ, deg | 70.142(2) |
| $V$, Å$^3$ | 4478.6(5) |
| $Z$ | 2 |
| $\rho_{calc}$, g/cm$^3$ | 1.325 |
| μ, mm$^{-1}$ | 0.703 |
| Reflections collected | 65147 |
| Independent reflections | 20622 |
| $R_{int}$ | 0.0347 |
| Reflections $I > 2\sigma(I)$ | 20622 |
| Parameters | 1090 |
| GOOF on $F^2$ | 1.029 |
| $R_1{}^a/wR_2{}^b$ ($I > 2\sigma(I)$) | 0.0529/0.1340 |
| $R_1{}^a/wR_2{}^b$ (all) | 0.0764/0.1496 |
| Largest diff. peak and hole, e Å$^{-3}$ | 1.373 and –0.810 |

$^a$ $R_1 = [\Sigma\ \mathrm{abs}(\mathrm{abs}(F_o) - \mathrm{abs}(F_c))]/\ [\Sigma\ \mathrm{abs}(F_o)]$. $^b$ $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\ \Sigma[w(F_o^2)^2]^{0.5}$.

in Table 1, selected bond lengths and angles are shown in Table 2.

Supplementary material for structure **I** has been deposited with the Cambridge Crystallographic Data Centre (no. 1912269; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

**Computational details.** Structure optimization (OPT) calculations were performed with the quantum chemistry program Gaussian 09 [53–55]. The 3-21G* basis set is used for C, H, P. Geometry optimization and HF energy were done with the functional of B3LYP.2-Butylene as the simplest *cis-trans* isomers were used for the comparison of *cis-trans* isomerism of Dppm.

## RESULTS AND DISCUSSION

The reaction equation of the complex preparation is observed in Scheme 2.

$$2Cu(CH_3CN)_4BF_4 + 4Dppm + NaCl \xrightarrow[70°C,\ 20\ h]{CH_3OH} I + NaBF_4 + 8CH_3CN$$

**Scheme 2.**

The title complex is air stable, and exhibits good solubility in common organic solvents such as acetonitrile and dichloromethane, however it is insoluble in ether and methanol. The IR spectroscopy results are consistent with its formulation. The IR spectrum of complex **I** exhibits broad bands at approximately 3396, 1435, and 1059 cm$^{-1}$, which correspond to the stretching frequencies of the C–H bond of phenyl and ylmethyl group, the C=C bond of phenyl group, and the B–F bonds of the tetrafluoroborate ($BF_4^-$),

**Table 2.** Selected bond lengths (Å) and angles (deg) for complex **I**

| Bond | $d$, Å | Bond | $d$, Å |
|---|---|---|---|
| Cu(1)–P(1) | 2.3156(9) | Cu(1)–P(3) | 2.3132(8) |
| Cu(1)–P(5) | 2.3127(8) | Cu(2)–P(2) | 2.3029(8) |
| Cu(2)–P(4) | 2.2967(8) | Cu(2)–P(7) | 2.3010(8) |
| Cu(1)–Cl(1) | 2.3894(8) | Cu(2)–Cl(1) | 2.4002(8) |
| Angle | ω, deg | Angle | ω, deg |
| P(5)Cu(1)P(3) | 120.05(3) | P(4)Cu(2)P(7) | 112.39(3) |
| P(5)Cu(1)P(1) | 105.89(3) | P(4)Cu(2)P(2) | 111.05(3) |
| P(3)Cu(1)P(1) | 112.63(3) | P(7)Cu(2)P(2) | 112.53(3) |
| P(5)Cu(1)Cl(1) | 104.41(3) | P(4)Cu(2)Cl(1) | 98.22(3) |
| P(3)Cu(1)Cl(1) | 109.93(3) | P(7)Cu(2)Cl(1) | 107.76(3) |
| P(1)Cu(1)Cl(1) | 102.20(3) | P(2)Cu(2)Cl(1) | 114.07(3) |
| P(1)C(1)P(2) | 114.37(16) | P(4)C(2)P(3) | 114.81(15) |
| P(5)C(3)P(6) | 118.23(17) | P(7)C(4)P(8) | 119.46(17) |
| Cu(1)Cl(1)Cu(2) | 94.73(3) | | |

respectively. The composition of **I** was also confirmed by NMR studies. In $^1$H NMR spectrum of complex **I** in methanol, two groups of proton peaks at 3.2 and 6.9~7.3 ppm with a 1 : 10 (~2 : 20) relationship between each other were consistent with the ylmethyl protons and the phenyl protons of Dppm ligands, respectively.

These results are similar with our previously reported complex $[Cu_2(\mu_2\text{-}\eta^1,\eta^1\text{Dppm})_2(\mu_2\text{-}\eta^1,\eta^1\text{-}FcCO_2)(CH_3CN)]BF_4 \cdot CH_3CN$ [22]. The electronic absorption spectrum of **I** in $CH_3CN$ exhibits a prominent band at 256 nm ($\varepsilon_{max} = 4.55 \times 10^4$ L mol$^{-1}$ cm$^{-1}$). Compared with the maximum absorption peaks of the free Dppm ligand at 234 nm ($\varepsilon_{max} = 2.33 \times 10^4$ L mol$^{-1}$ cm$^{-1}$, 208 nm ($\varepsilon_{max} = 2.88 \times 10^4$ L mol$^{-1}$ cm$^{-1}$), nearly 30 nm red shift has been occurred in the UV range. We can infer that the maximum absorption peak of complex **I** can be assigned to the $\pi$–$\pi^*$ transition perturbed by the coordination interactions of Cu and P. Prior to the measurement of thermal stability and fluorescence property of this complex, PXRD data were recorded for the identification of the phase of the powder sample.

The solid-state structure of the title complex crystallizes as a dinuclear copper(I) complex in the triclinic space group $P\bar{1}$ (Table 1) and can be described as a discrete cationic $[(\mu_2\text{-}\eta^1,\eta^1\text{-}cis\text{-Dppm})_2Cu_2(\eta^1\text{-}trans\text{-Dppm})_2(\mu_2\text{-Cl})]^+$ species (Fig. 1a) and one isolated $BF_4^-$ counter anions. Its main structure consists of two tetrahedron coordinated copper(I) atoms, which are bridged by a pair of *cis*-Dppm molecules and one chloride ion, and two *trans*-Dppm molecules in mono-dentate fashion. The eight-membered $Cu_2C_2P_4$ ring of $\{Cu(\mu_2\text{-}\eta^1,\eta^1\text{-}trans\text{-Dppm})_2Cu\}$ unit shows the boat–boat conformation [20, 21], whereas the $\mu_2$ chloride ion locates in its opposite center (Fig. 1b). Similar core structure can be found in the reported complexes, like $[Cu_2(Dppm)_2(Dmcn)(Cl)_2] \cdot 2Dmcn$ (Dmcn = dimethylcyanamide) [18], $[Cu_2(Dppm)_2(C_9H_7N)Cl_2] \cdot (C_9H_7N)_2 \cdot H_2O$ ($C_9H_7N$ = quinoline) [15] and so on. The Cu(1)–Cu(2) distance is 3.5237(5) Å for complex **I**, which is above the sum of van der Waals radii for copper (2.8 Å), and is longer than the longest distance (3.4666(7) Å) in three determined $\{Cu(\mu_2\text{-}\eta^1,\eta^1\text{-}cis\text{-Dppm})_2(\mu_2\text{-Cl})Cu\}$ units [15, 18]. Obviously, the longest copper–copper distance generates a bigger core structure, which provides the possibility for incorporating other ligands with increasing steric hindrance. Each copper(I) atom further coordinates with one unidentate *trans*-Dppm on both sides of the core structure. The 1 : 2 ratio of copper to Dppm represents the lowest percentage among all Cu-Dppm complexes.

For better understanding why the Dppm ligands adopt two different coordination styles in one coordination compound, via calculation we optimized the structures of *trans*-, *cis*-Dppm and *trans*-, *cis*-2-butylene for comparison (Table 3). The calculation results show that energy barrier of the *cis*-*trans* isomerization of Dppm is $1.19 \times 10^{-3}$ a.u. over a thousand times lower than 2-butylene (1.13 a.u.). The great difference in HF energies between complex **I** and 2-butylene is indicated that although the *trans*-configuration of Dppm is energy-favored, the energy barrier among *trans*- and *cis*-Dppm is so small that they can easily isomerize. In the case of complex **I**, when Dppm coordinated with two metal centers they tend to adopt $\mu_2$-$\eta^1,\eta^1$-*cis*-Dppm coordination mode, whereas when

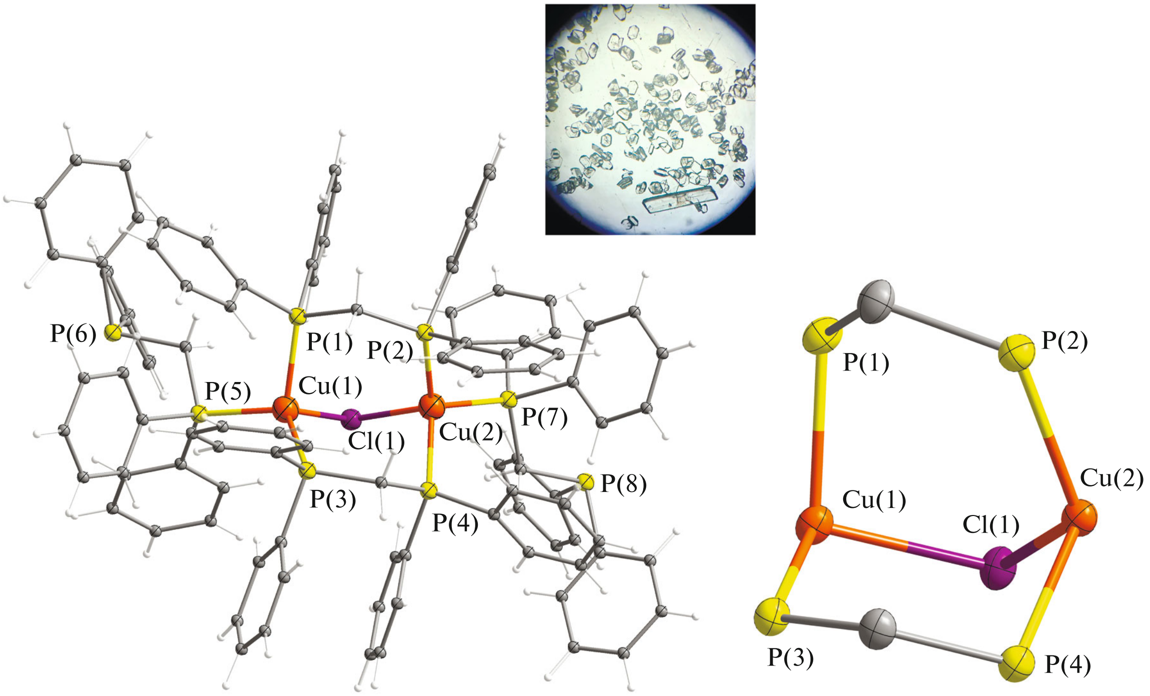
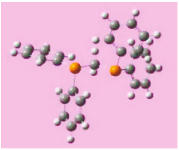
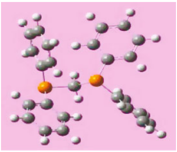
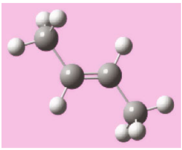
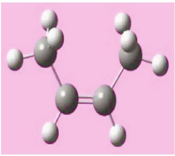


**Fig. 1.** The molecular structure and selected atom labelling of $[(\mu_2\text{-}\eta^1,\eta^1\text{-}cis\text{-Dppm})_2Cu_2(\eta^1\text{-}trans\text{-Dppm})_2(\mu_2\text{-Cl})]^+$, the photo of crystals **I** is in the top right corner (a); the core structure of $\{Cu(\mu_2\text{-}\eta^1,\eta^1\text{-}cis\text{-Dppm})_2(\mu_2\text{-Cl})Cu\}$ unit (b).

Dppm coordinated with one metal center $\eta^1$-*trans*-Dppm coordination mode is favored.

The thermal stability of complex **I** was investigated by TG measurement (Fig. 2a) and PXRD analysis (Fig. 2b), carried out on an as-synthesized powder sample. From the TGA curve and the XRD pattern at 355°C, we can infer that up to 355°C the main structure of complex **I** is still maintained. One main mass-loss step during the decomposition of the complex is observed between 355 and 445°C. In this step, the

**Table 3.** The comparison of the OPT structures and HF energy between Dppm and 2-butylene

| Types of ligands | OPT structure and HF, a.u. | |
|---|---|---|
| Dppm | <br>*trans*-Dppm<br>HF = –1640.0642773 | <br>*cis*-Dppm<br>HF = –1640.0630868 |
| 2-Butylene | <br>*trans*-2-Butylene<br>HF = –156.3684473 | <br>*cis*-2-Butylene<br>HF = –155.2405729 |

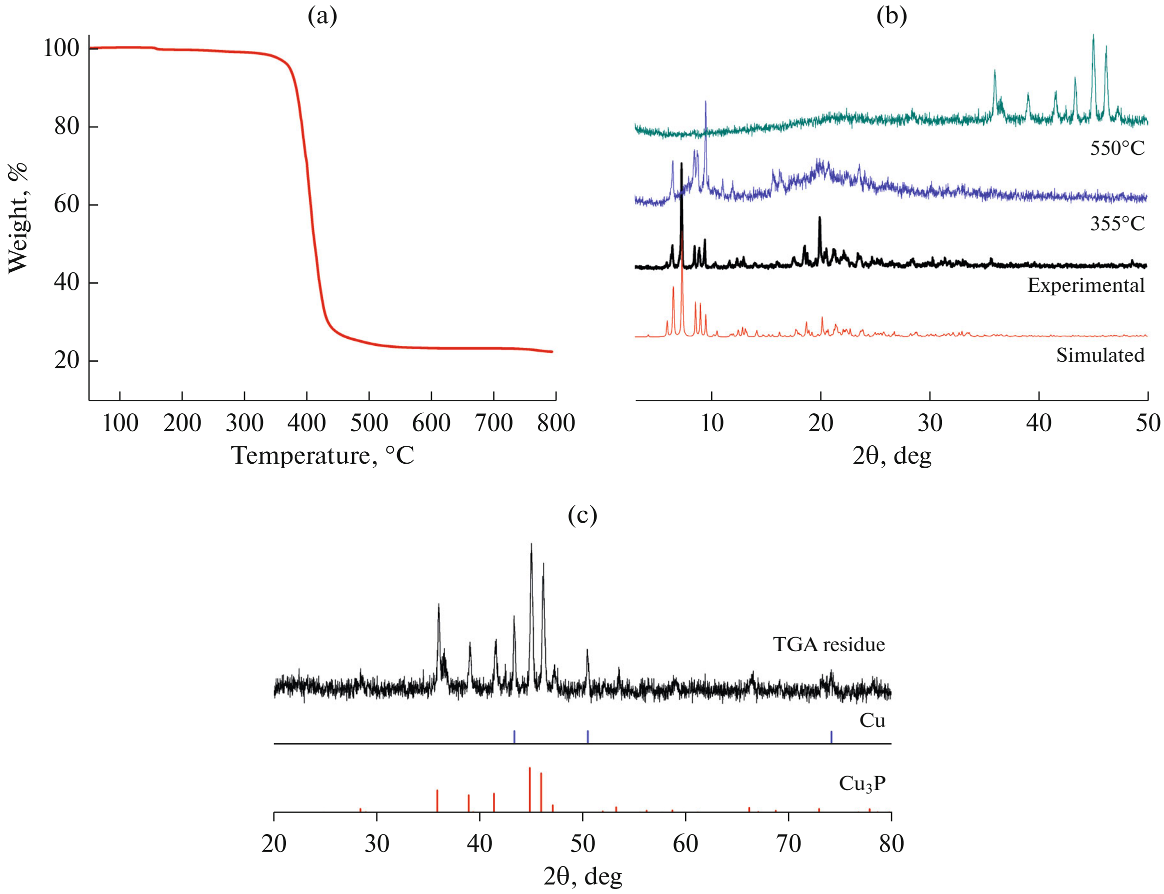


**Fig. 2.** The TGA curve of complex **I** (a); powder XRD analysis of its thermal decomposition to 550°C (b) and TGA residue (c).

organic part of complex **I** is completely decomposed. The remains of the decomposed product are presupposed to be a mixture of $Cu_3P$ and Cu (Fig. 2c). All results show that complex **I** possesses better thermal stability than our previously reported heterometallic complex [22].

The solid-state UV–Vis absorption spectrum (Fig. 3a) of complex **I** was recorded on an as-synthesized powder sample. In the solid state, complex **I** exhibits strong absorption in the near UV region, this is line with the results which observed in complex $[Cu_4(\mu_2\text{-Dppm})_4(CN)_2](PF_6)_2$ [19]. The solid UV–Vis diffuse reflectance spectrum (Fig. 3b) showed the optical energy gap of **I** to be 2.66 eV, which is consistent with the color of complex **I** (colorless). The color is similar with other cuprous complexes via various phosphine ligands [37, 56].

Complex **I** exhibits room temperature cyan photoluminescence in the solid state with quantum yield of 1.87%. In the solid state complex **I** (Fig. 4) shows emission maxima at a wavelength of 481 nm with a shoulder peak at 511 nm. The photoluminescence of related copper(I) complexes were intensively studied in literature, it's normal for a cyan emission in those complexes. Like several $Cu_2(Dppm)_2$ complexes [14], the high-energy emissions bands (481 nm) are tentatively assigned as an intraligand phosphine excited state. Based on the structure and photophysical properties comparison with series of copper-Dppm-Cl complexes, [14, 26] the low-energy emissions bands (511 nm) are more likely assigned as an MLCT transition between metal *d*-orbitals with contributions from the phosphorous atoms or the chloride ion.

In conclusion, we describe herein the synthesis and properties of a new binuclear copper(I)-Dppm complex. The complex has been characterized by various spectroscopic techniques and single crystal X-ray crystallography. In addition, its room temperature cyan photoluminescence in the solid state has been observed. To the best of our knowledge, complex **I** represents the first binuclear copper(I)-Dppm complex with the minimum copper to Dppm ratio (1 : 2).

## SUPPLEMENTARY MATERIAL

Supplementary materials are available for this article at https://doi.org/10.1134/S1070328420070052 and are accessible for authorized users.

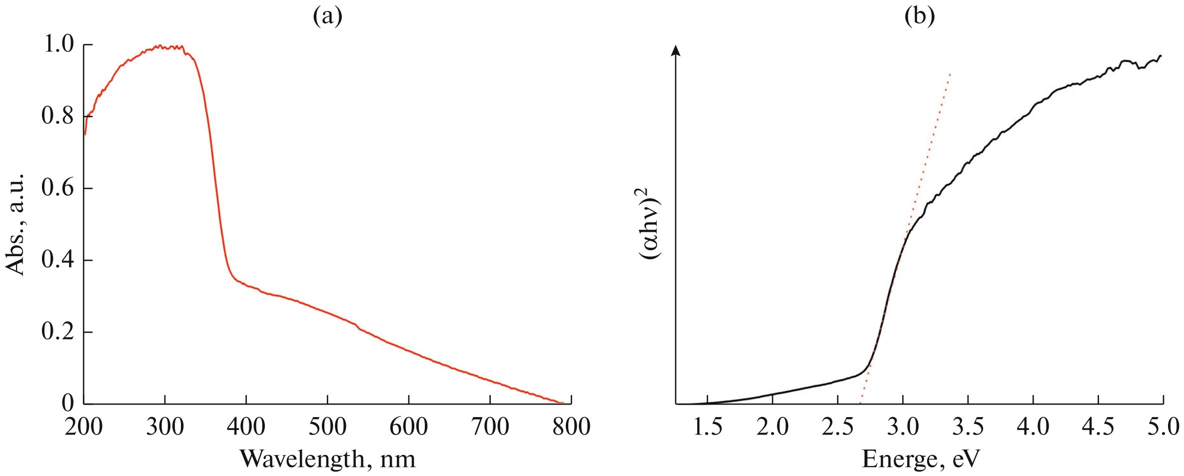


**Fig 3.** The solid-state UV–Vis absorption spectrum (a) and diffuse reflectance spectrum of complex **I** (b).

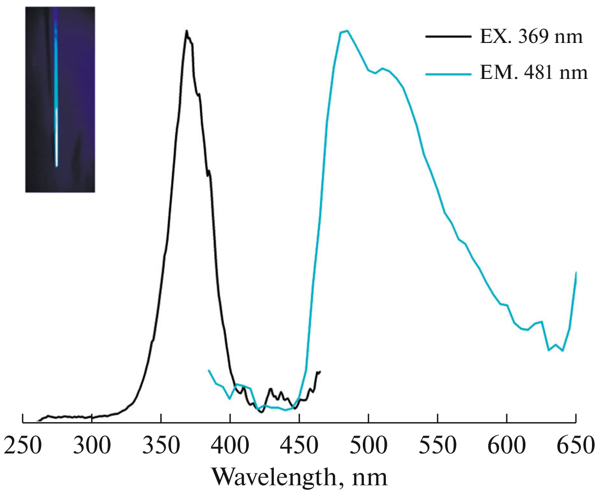


**Fig. 4.** The solid-state photoluminescence spectrum of complex **I** (the photoluminescence photo of complex **I** is in the top left corner).

## FUNDING

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