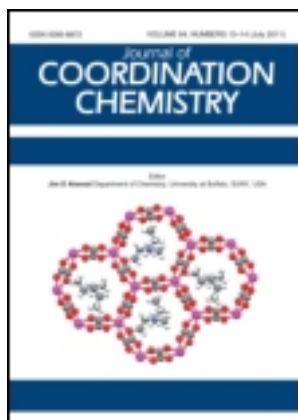


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Luminescent triply-bridged dicopper(I) complex possessing 3,5-bis{6-(2,2'-dipyridyl)}pyrazole as a bis-chelating ligand

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Luminescent triply-bridged dicopper(I) complex possessing 3,5-bis{6-(2,2'-dipyridyl)}pyrazole as a bis-chelating ligand

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A new triply-bridged dicopper(I) complex, $[\text{Cu}_2(\mu\text{-dppm})_2(\mu\text{-HL})](\text{NO}_3)_2$ (**1**), has been prepared *via* successive treatment of cupric nitrate trihydrate with bis(diphenylphosphino)methane (dppm) and 3,5-bis{6-(2,2'-dipyridyl)}pyrazole (HL) in 2:4:1 molar ratio in dichloromethane. X-ray diffraction analysis of **1** reveals that the two Cu(I)s are in highly distorted tetrahedral environments with a distance of 4.2775(10) Å, triply bridged by two dppm ligands and one HL chelate as a bis-bidentate bridging ligand through two bipyridyl moieties. Intermolecular $\text{N}\cdots\text{H}-\text{C}$ hydrogen bonding and $\pi\cdots\text{H}-\text{C}$ interactions assemble the $[\text{Cu}_2(\mu\text{-dppm})_2(\mu\text{-HL})]^{2+}$ cations into a 3-D supramolecular architecture with extended channels along the *b*-axis, filled with methanol and anions. Complex **1** shows weak low-energy absorptions at 350–425 nm, tentatively ascribed to Cu(I) to HL metal-to-ligand charge-transfer (MLCT) transition, probably mixed with some ILCT character inside HL. The emission is observed at ambient temperature for **1**, both in solution and in the solid state, originating from the MLCT excited states.

Keywords: Copper(I) complex; Crystal structure; 3,5-Bis{6-(2,2'-dipyridyl)}pyrazole; Bis(diphenylphosphino)methane; Photoluminescence

1. Introduction

Copper(I) complexes receive attention due to their structural diversity and intriguing photophysical properties with promising applications in electroluminescent devices, luminescence-based sensors, biological labeling, and solar energy capture [1–6]. Many copper(I) complexes bearing diimine and phosphine ligands are air-stable and highly emissive in both solution and solid states [7–9]. The auxiliary phosphine plays a key role in stabilizing the Cu(I) center, albeit not involved in the metal-to-ligand charge-transfer (MLCT) transition, and has a significant impact on the photophysical properties of cuprous complexes [4, 7, 10–14].

Recently, we initiated the synthesis of phosphorescent Cu(I) complexes featuring the 3,5-bis{6-(2,2'-dipyridyl)}pyrazole (HL) ligand [15]. The results indicated that ancillary

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ligands such as halide have important effects on the solid-state photoluminescence properties of HL-based dicopper(I) complexes. Unfortunately, however, the two luminescent Cu(I)–HL complexes are insoluble in commonly used organic solvents, which is a disadvantage to device fabrication. Therefore, to find out more about HL and its copper(I) derivatives, and hence to improve the electronic and physical properties of HL-based copper(I) complexes, it is desirable to synthesize more luminescent Cu(I)–HL complexes utilizing phosphine as the ancillary ligand. The introduction of highly encumbered phosphine might bring improvement for solubility and photoluminescence properties of the resulting copper(I)–HL complexes.

Herein, we describe the synthesis, crystal structure, and photophysical properties of a new triply-bridged dicopper(I) complex with 3,5-bis{6-(2,2'-dipyridyl)}pyrazole (HL), $[\text{Cu}_2(\mu\text{-dppm})_2(\mu\text{-HL})](\text{NO}_3)_2$ (**1**), using bis(diphenylphosphino)methane (dppm) as the auxiliary bridging ligand.

2. Experimental

2.1. General procedures and materials

Commercially available reagents were used without purification unless otherwise stated. Solvents used in spectroscopic analysis were freshly distilled over appropriate drying reagent under N_2 . 3,5-Bis{6-(2,2'-dipyridyl)}pyrazole (HL) was prepared according to the literature method [15–18]. Bis(diphenylphosphino)methane (dppm) was purchased from Alfa Aesar.

2.2. Physical measurements

Elemental analyses (C, H, N) were carried out on a Perkin-Elmer model 240C elemental analyzer. Fourier transform infrared (FTIR) spectrum was recorded on a Nicolet 5700 FT-IR spectrometer using a KBr pellet. Electronic absorption spectra in dichloromethane solutions were measured on a Perkin-Elmer Lambda 25 UV-Vis spectrometer. Emission spectra were recorded on a Perkin-Elmer LS 55 luminescence spectrometer with a red-sensitive photomultiplier type R928.

2.3. Synthesis of $[\text{Cu}_2(\mu\text{-dppm})(\mu\text{-HL})](\text{NO}_3)_2$ (**1**)

A mixture of bis(diphenylphosphino)methane (56.4 mg, 0.147 mmol) and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (17.6 mg, 0.073 mmol) in dichloromethane (25 mL) was stirred for 4 h at ambient temperature. To this colorless transparent solution was added dropwise with stirring a solution of 3,5-bis{6-(2,2'-dipyridyl)}pyrazole (HL) (13.2 mg, 0.035 mmol) in dichloromethane (5 mL), giving a light yellow solution, which was stirred for 3 h. The reaction mixture was evaporated at reduced pressure to give a light-yellow residue. Pure light-yellow crystals were obtained by slow diffusion of diethyl ether into a dichloromethane/methanol (3:1) mixture over a few days. A suitable crystal was chosen for single-crystal X-ray diffraction analysis. Yield: 31.6 mg, 0.022 mmol, 63% (based on the HL ligand). Elemental Anal. Calcd for

Table 1. Crystallographic data for **1**.

Empirical formula	C ₇₄ H ₆₄ Cu ₂ N ₈ O ₇ P ₄
Formula weight	1428.31
Temperature (K)	293(2)
Radiation (λ , Å)	0.71073
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Unit cell dimensions (Å)	
<i>a</i>	20.4888(6)
<i>b</i>	14.7778(5)
<i>c</i>	21.4233(6)
Volume (Å ³), <i>Z</i>	6486.5(3), 4
Calculated density, ρ_{Calcd} (g cm ⁻³)	1.463
μ (mm ⁻¹)	0.819
<i>F</i> (000)	2951
Crystal size (mm ³)	0.300 × 0.280 × 0.200
θ range for data collection (°)	1.38–27.45
Limiting indices	–26 ≤ <i>h</i> ≤ 18; –19 ≤ <i>k</i> ≤ 19; –27 ≤ <i>l</i> ≤ 24
Reflections collected/unique	32,980/7674 [<i>R</i> (int) = 0.0874]
Completeness to $\theta = 27.45$ (%)	99.7
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	7674/0/487
Goodness-of-fit	0.971
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0594, 0.1406
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1398, 0.1867
Largest difference peak and hole (e Å ⁻³)	1.612 and –0.579

C₇₃H₆₀Cu₂N₈O₆P₄·CH₃OH (%): C, 62.23; H, 4.52; N, 7.84. Found (%): C, 62.54; H, 4.40; N, 7.92. Selected IR (KBr, cm⁻¹): 3419, 3055, 2922, 2853, 1641, 1595, 1569, 1463, 1433, 1387, 1342, 1312, 1225, 1095, 1033, 999, 968, 827, 785, 741, 692, 515, 476.

2.4. X-ray crystallography

A single-crystal suitable for data collection was selected and glued to the tip of a glass fiber. X-ray diffraction data were measured on a Bruker SMART CCD area detector using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structure was solved by direct methods using SHELXS-97 [19], and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogens were placed in idealized geometries and their contributions were added to the structure factor calculations. Full-matrix least-squares refinement was based on *F*² with SHELXL-97 [20]. The detailed crystal data and structure refinement parameters of **1** are summarized in table 1, and selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. Synthesis

This project was carried out to prepare luminescent dicopper(I) complexes featuring 3,5-bis{6-(2,2'-dipyridyl)}pyrazole (HL) as a bis-chelating bridge. Dicopper(I) halide complexes bridged by the HL ligand show that the halide exerts an important influence

Table 2. Selected bond distances (Å) and angles (°) for **1**.

Cu1–P1	2.2647(11)	N1–Cu1–N2	80.68(19)
Cu1–N1	2.081(5)	N1–Cu1–P1	101.92(4)
Cu1–N2	2.148(5)	N2–Cu1–P1	100.68(4)
Cu2–P2	2.2691(11)	P1–Cu1–P1#1	150.14(6)
Cu1–N6	2.077(5)	N1–Cu1–Cu2	164.13(15)
Cu1–N5	2.155(5)	N2–Cu1–Cu2	115.18(12)
Cu1...Cu2	4.2775(10)	P1–Cu1–Cu2	76.07(3)
		N6–Cu2–N5	80.3(2)
		N6–Cu1–P2	103.38(4)
		N5–Cu1–P2	100.55(4)
		P2–Cu1–P2#1	148.23(6)
		N6–Cu2–Cu1	162.38(15)
		N5–Cu2–Cu1	117.29(13)
		P2–Cu2–Cu1	74.65(3)

Symmetry transformations used to generate equivalent atoms, #1: $x, -y + 3/2, z$.

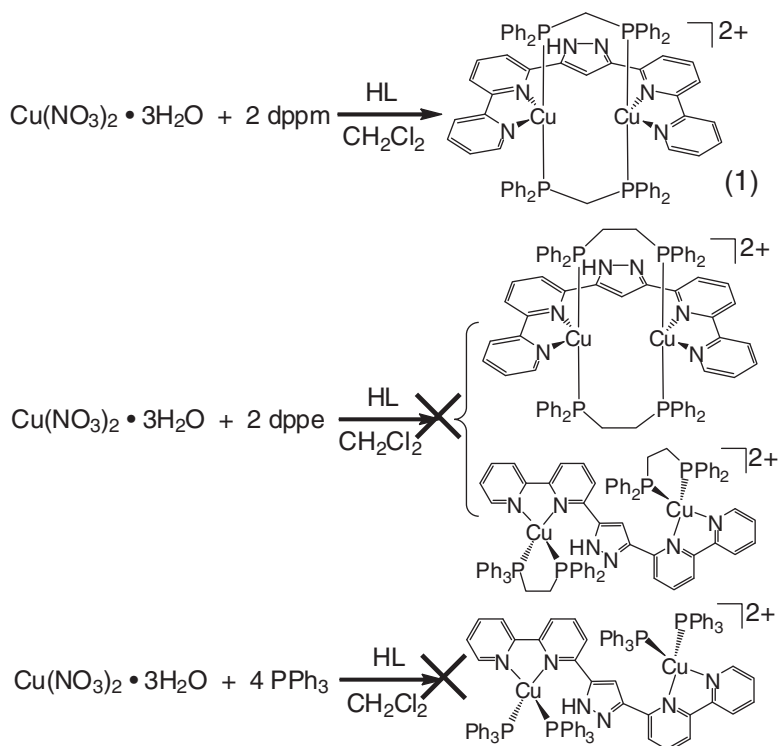
on photoluminescence [15]. For further investigation on the nature of HL and its Cu(I) derivatives, we proceeded to synthesize HL-based Cu(I) complexes with the formula $[\text{Cu}_2(\text{P}_2)_2(\mu\text{-HL})](\text{NO}_3)_2$ (P_2 denotes two PPh_3 or one diphosphine ligand), which might be distinct from the two HL-based predecessors due to the encumbered phosphine ligand introduced. Furthermore, we expected replacement of the halide with the phosphine to significantly affect the geometric and physical properties of the synthesized cuprous complexes.

An unexpected dicopper(I) complex $[\text{Cu}_2(\mu\text{-dppm})_2(\mu\text{-HL})](\text{NO}_3)_2$ (**1**), instead of an anticipated dicopper(I) species $[\{\text{Cu}(\text{dppm})\}_2(\mu\text{-HL})](\text{NO}_3)_2$, was isolated as the light-yellow product *via* the treatment of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ with two equivalents of dppm in dichloromethane, followed by addition of 0.5 equivalent of 3,5-bis{6-(2,2'-dipyridyl)}pyrazole (HL), where dppm not only served as a bridging ligand, but also as a reducing agent of Cu(II). Pure crystalline product of **1** was afforded by the slow diffusion of diethyl ether into its dichloromethane/methanol (3:1) mixture in several days. As expected, the solubility of **1** has significant amelioration relative to the two insoluble halide predecessors [15]. The crystalline product of **1** is easily soluble in methanol, although it is only slightly soluble in other common solvents such as ethanol, dichloromethane, chloroform, acetonitrile, and acetone.

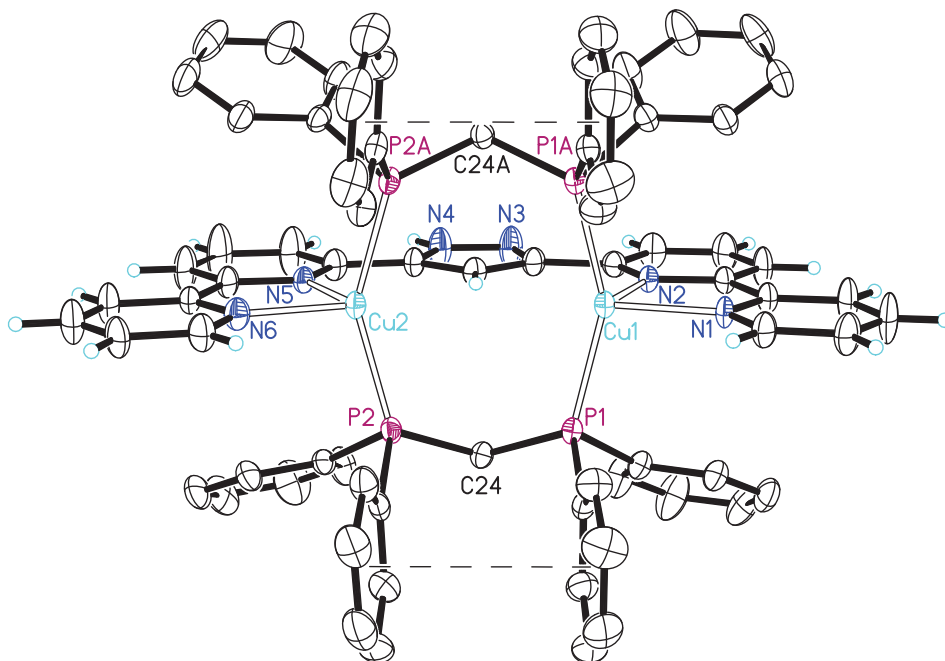
Utilizing 1,2-bis(diphenylphosphino)ethane (dppe) instead of dppm, according to the procedures similar to **1**, we failed to obtain $[\text{Cu}_2(\mu\text{-dppe})_2(\mu\text{-HL})](\text{NO}_3)_2$ and $[\{\text{Cu}(\text{dppe})\}_2(\mu\text{-HL})](\text{NO}_3)_2$ (scheme 1). Similarly, we have also been unsuccessful in preparing HL-based dicopper(I) complex $[\{\text{Cu}(\text{PPh}_3)_2\}_2(\mu\text{-HL})](\text{NO}_3)_2$ using PPh_3 instead of dppm. It is suggested that the appropriate choice of phosphine ligand is crucially important for the construction of HL-based Cu(I) phosphine complexes.

3.2. Crystal structure

Crystal structure of **1** consists of a binuclear cation $[\text{Cu}_2(\mu\text{-dppm})_2(\mu\text{-HL})]^{2+}$, anions, and solvated methanol. The perspective view of the cation with atom-labeling scheme is depicted in figure 1. In the binuclear cation, the two copper(I)s are maintained at a separation of 4.2775(10) Å by three bridging ligands, two dppm, and one HL chelate



Scheme 1. Synthetic route of HL-based dicopper(I) complexes.

Figure 1. ORTEP drawing of **1** with atom-labeling scheme showing 30% probability thermal ellipsoids and intramolecular π - π interactions (dashed lines) between phenyl rings of dppm. Anions, methanol and hydrogens of dppm are omitted for clarity.

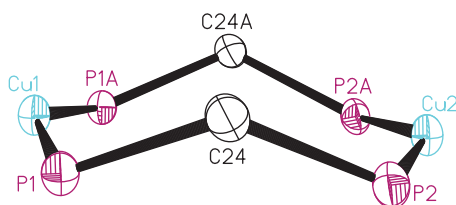


Figure 2. View of the eight-membered $\text{Cu}(\mu\text{-dppm})_2\text{Cu}$ ring showing the chair–chair conformation.

acting as a tetradentate binucleating bridge *via* N1, N2, N5, and N6 from two bipyridyl moieties. As a consequence of the constraint of the 3,5-pyrazolyl spacer of HL, intramolecular $\text{Cu}(\text{I}) \cdots \text{Cu}(\text{I})$ distance (4.2775(10) Å) is slightly shorter than that (4.671 and 4.747 Å) of $[\text{Cu}_2(\mu\text{-dppm})_2(\text{bpy})_2](\text{BF}_4)_2$ [21] and $[\text{Cu}_2(\mu\text{-dppm})_2(\text{SiMe}_3\text{C}\equiv\text{C}\text{bpyC}\equiv\text{CSiMe}_3)_2](\text{ClO}_4)_2$ [22], but markedly much longer than those (≤ 3.420 Å) found in other dicopper complexes bearing the $[\text{Cu}_2(\mu\text{-dppm})_2]$ unit [23–25]. In fact, **1** can be regarded as two 2,2'-bipyridyl fragments of $[\text{Cu}_2(\mu\text{-dppm})_2(\text{bpy})_2]^{2+}$ linked by one 3,5-pyrazolyl bridge in the 6-position of 2,2'-bipyridyl. Both four-coordinated Cu(I)s are in a highly distorted tetrahedron constituted by two phosphorus of dppm ligands and two nitrogens from bipyridyl groups, with the P–Cu–P angles of 150.14(6) and 148.23(6)°, which are much larger than those reported [21–26], coming probably from a combination of the electronic and steric effects between the phenyl groups of dppm and the rigidity of HL. The small N–Cu–N angles (80.68(19) and 80.3(2)°) from the constraint of the bite angles of bipyridyl units are comparable to those in other copper(I) diimine complexes [21, 22, 26–30]. Weak intramolecular $\pi \cdots \pi$ contacts are also observed between phenyl rings of dppm (center-to-center distance 3.640 Å, figure 1) [31].

Different from the eight-membered $\text{Cu}(\mu\text{-dppm})_2\text{Cu}$ rings of $[\text{Cu}_2(\mu\text{-dppm})_2(\mu\text{-PPDMe})]^{2+}$ (PPDMe = 3,6-bis(3,5-dimethylpyrazol-1-yl)pyridazine) [32] and $[\text{Cu}_2(\mu\text{-dppm})_2(\mu\text{-mpyO})]^+$ (mpyO = 6-methylpyridin-2-olate) [33] adopting the boat–chair and boat–boat conformations, respectively, the corresponding dicopper ring of **1** exhibits an apparent chair–chair conformation (figure 2). In addition, the 12-membered bimetallacycle consisting of Cu1, P1, C24, P2, Cu2, N5, C14, C13, C12, C11, C10, and N2 from dppm and HL was found in **1**, which is also observed in $[\text{Cu}_2(\mu\text{-dppm})_2(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})](\text{BF}_4)_2$ ($\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ = 1-methyl-3,5-di(2-pyridyl)benzene) where both Cu(I)s are three coordinate [28]. The dihedral angle between Cu1P1P2Cu2 and HL planes of **1** is 85.229(26)°, close to the ideal right-angle, and much larger than those in analogous $[\text{Cu}_2(\mu\text{-dppm})_2]$ -based complexes [23, 24, 32–35]. The Cu–P and Cu–N lengths (average 2.27 and 2.12 Å, respectively) are in the range typical of four-coordinate Cu(I) complexes [7–14]. Akin to the reported dicopper(I) halide complexes bearing the same HL [15], the Cu–N distances (2.148(5) and 2.155(5) Å) for the inner pyridine rings of HL are somewhat longer than Cu–N distances (2.081(5) and 2.077(5) Å) of the peripheral pyridine rings as a result of electronic and steric effects of dppm and HL.

A crystallographic mirror plane bisects the cation through HL and two copper(I)s. HL is virtually coplanar with the Cu(I)s, but is not axisymmetric in the crystal lattice due to weak intermolecular hydrogen-bonding interactions (N3 \cdots H2A 2.782 Å, N3–H2A–C2 179.14°) between pyrazolyls of the neighboring binuclear cations, and through

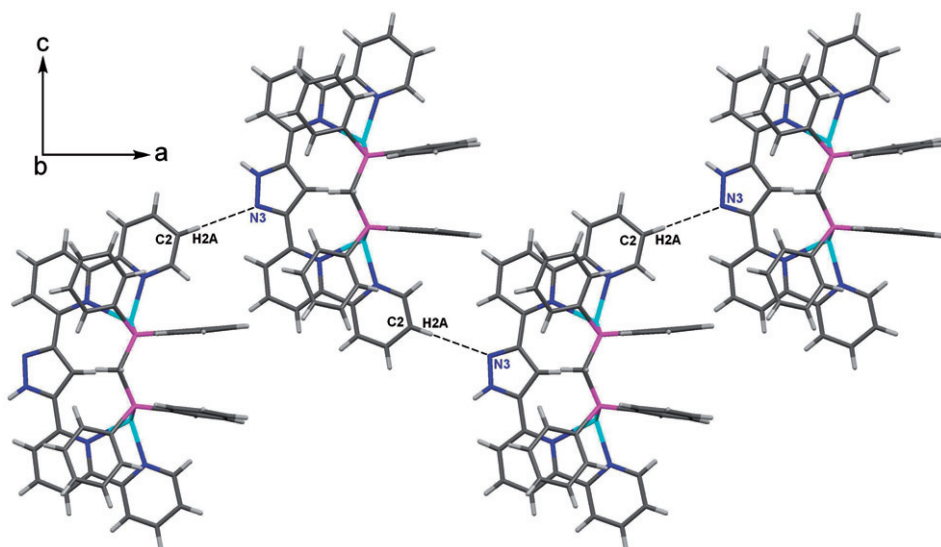


Figure 3. View of a 1-D zigzag arrangement along the *a*-axis generated by intermolecular N \cdots H-C hydrogen bonds (dashed lines).

which a 1-D zigzag array is generated along the *a*-axis (figure 3). These adjacent zigzag chains further interact *via* short intermolecular C-H \cdots π interactions (2.75–3.0 Å) between phenyl rings of dpmp (figure 4), resulting in a 3-D architecture with extended channels along the *b*-axis (figure 5), filled by methanol and anions.

3.3. Photophysical properties

Supplementary material provides the absorption spectra of **1** and HL in dichloromethane at ambient temperature. HL displays two absorptions at $\lambda_{\text{max}} \approx 265$ and 309 nm, attributed to $\pi \rightarrow \pi^*$ transitions inside HL. Complex **1** exhibits multiple absorptions ($\epsilon > 10^4$ (mol L $^{-1}$) $^{-1}$ cm $^{-1}$) in the 235–350 nm region, which most likely originated from HL and dpmp. There is a good match of the absorption spectra in high-energy region (≤ 350 nm) of HL and **1**. The red shift of the π - π^* absorption peaks of **1** is consistent with better conjugation of the coordinated HL relative to free HL, leading to a smaller π - π^* energy gap. In addition to the high-energy absorption bands, **1** has a comparatively weak low-energy absorption tail ($\epsilon < 9 \times 10^3$ (mol L $^{-1}$) $^{-1}$ cm $^{-1}$) at 350–425 nm, which can be identified as the MLCT transition from the d_{π} orbital of Cu(I) to the unoccupied π^* orbital of HL, probably mixed with some intraligand charge-transfer character inside HL.

The photoluminescence properties of HL and **1** are investigated at ambient temperature (figure 6). HL emits a purple color with $\lambda_{\text{max}} \approx 355$ nm in dichloromethane, attributed to the fluorescent emission stemming from ligand-centered $\pi \rightarrow \pi^*$ transition. **1** displays a single, broad, structureless solid-state emission band centered at 517 nm. From previous work [3–5, 7–15, 36], the highest occupied molecular orbital (HOMO) of **1** is principally on copper(I), probably including some contributions from the diphosphine ligands and a small contribution from HL. Its lowest-unoccupied

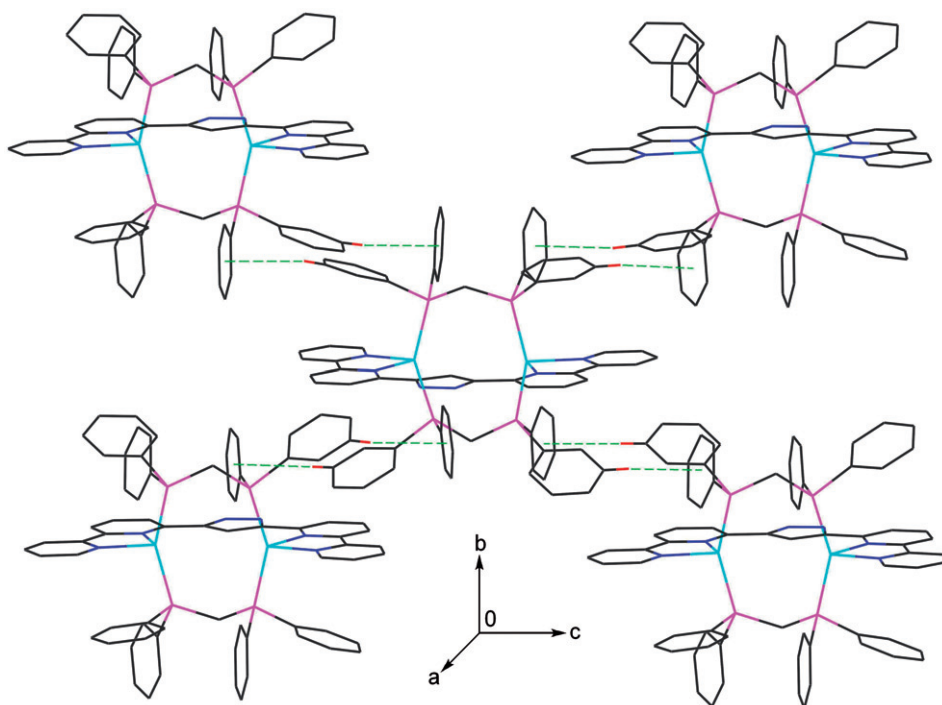


Figure 4. Intermolecular C-H... π interactions (dashed lines) between adjacent cations in 1.

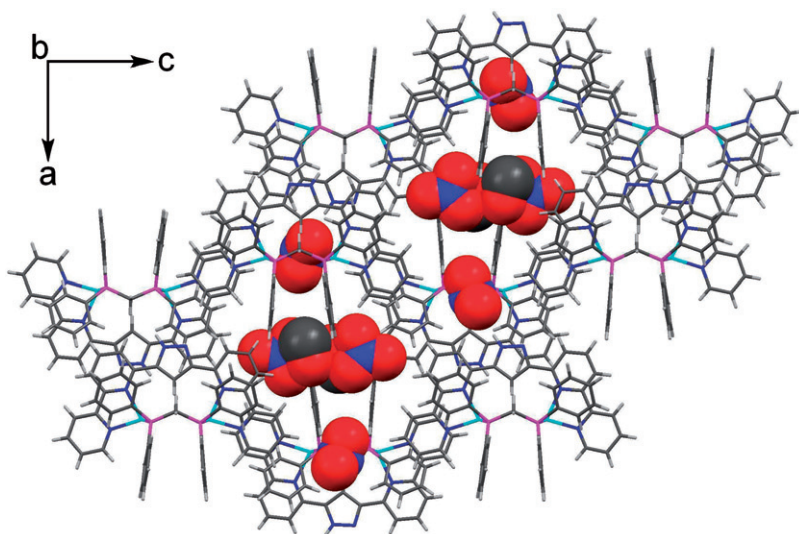


Figure 5. View of 1 along the *b*-axis. The cation of 1 is depicted in stick style and both anions and methanol are displayed in space-filling style.

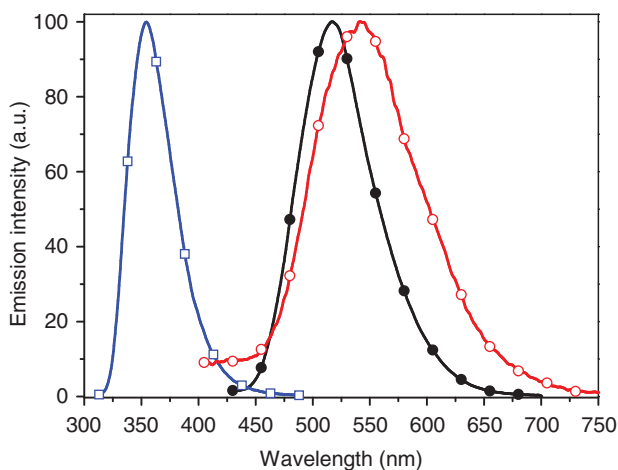


Figure 6. Emission spectra of HL in dichloromethane (—□—) and **1** in methanol (—○—) and in the solid state (—●—) at ambient temperature.

molecular orbital (LUMO) is believed to be primarily localized on HL. Thus the lowest-lying emissive excited state of **1** is best regarded as the $^3\text{MLCT}$ character from $d(\text{Cu}) \rightarrow \pi^*(\text{HL})$. The emission energy (λ_{max} , 517 nm) of **1** is much higher than that (λ_{max} , 622 and 638 nm for the iodide and bromide complexes, respectively) of HL-based dicopper(I) halide species. Such a large blue-shifting of 105–121 nm can be rationalized due to the replacement of halide *via* the good π -acceptor dppm, resulting in a lowering of the HOMO energy level, less influencing the LUMO energy, and hence leading to an increase of the HOMO–LUMO energy gap. Despite $[\text{Cu}_2(\mu\text{-dppm})_2(\text{bpy})_2](\text{BF}_4)_2$ being non-emissive in solution at room temperature [21], **1** exhibits a single, broad, structureless emission with maximum at 543 nm in degassed methanol solution at ambient temperature, most likely from both the constraint of the 3,5-pyrazolyl group of HL and intramolecular phenyl/phenyl $\pi \cdots \pi$ interactions of the dppm ligands, effectively impeding geometric relaxation and solvent attack. In the solid state, the emission (λ_{max} , 517 nm) of **1** has a small blue-shift of 16 nm at ambient temperature relative to that (λ_{max} , 533 nm) of $[\text{Cu}_2(\mu\text{-dppm})_2(\text{bpy})_2](\text{BF}_4)_2$ [21], probably due to the introduction of the 3,5-pyrazolyl linker, raising the LUMO level, and thus slightly increasing the HOMO–LUMO gap.

4. Conclusion

In summary, a new luminescent triply-bridged dicopper(I) complex with the tetradentate binucleating ligand 3,5-bis{6-(2,2'-dipyridyl)}pyrazole (HL), $[\text{Cu}_2(\mu\text{-dppm})_2(\mu\text{-HL})](\text{NO}_3)_2$ (**1**), was synthesized and structurally characterized. A 3-D architecture with extended channels along the *b*-axis was formed *via* weak intermolecular interactions involving $\text{N} \cdots \text{H}$ and $\pi \cdots \text{H}$ contacts, filled with anions and methanol. Substitution of halide with the phosphine ligand improves solubility and photophysical properties of HL-based dicopper(I) species. Differing from the insoluble

dicopper(I) halide predecessors of HL, **1** is easily soluble in methanol and displays a single, broad, structureless emission profile in both solution and solid states at ambient temperature, typical of phosphorescence from a ³MLCT excited state. The results reported herein provide some useful information for further design of luminescent multinuclear cuprous complexes based on 3,5-bis{6-(2,2'-dipyridyl)}pyrazole.

Supplementary material

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre with the deposition number of CCDC 808294 for **1**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk/deposit>).

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