

Syntheses, crystal structures and fluorescent properties of *R,R*-DIOP based copper (I) and cadmium (II) complexes {*R,R*-DIOP = (4*R*,5*R*)-*trans*-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxalane}

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ABSTRACT

Two chiral complexes, [CuCl(*R,R*-DIOP)]₂ (**1**) and [CdCl₂(*R,R*-DIOP)]_n (**2**), have been synthesized by reaction of CuCl or CdCl₂ with chiral diphosphine ligand *R,R*-DIOP under argon. They were characterized by elemental analysis, IR, UV–vis, fluorescence spectra and single-crystal X-ray diffraction. X-ray analysis indicates that the metal centers (Cu^I for **1** and Cd^{II} for **2**) are both in distorted tetrahedral environment, but **1** is a binuclear complex in which Cu^I ions are surrounded by two μ₂-bridging chloride ions and two bisonodentate coordinated *R,R*-DIOP ligands; while **2** is a helical polymer along *b* axis and each Cd^{II} ion is coordinated with two chloride ions and two P atoms of two μ₂-bridging *R,R*-DIOP ligands. Both of them crystallize in monoclinic system, space group P 2₁, with *a* = 9.8855(7) Å, *b* = 37.857(3) Å, *c* = 23.9585(16) Å, β = 92.0920(10)°, *Z* = 6 for (**1**) and *a* = 10.1740(8) Å, *b* = 13.9899(11) Å, *c* = 11.4007(9) Å, β = 108.3690(10)°, *Z* = 2 for (**2**). Fluorescence measurements show that complex **1** can emit much strong blue emission than **2** at room temperature in the solid state.

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1. Introduction

The chiral phosphine compound *R,R*-DIOP = (4*R*,5*R*)-*trans*-4,5-bis(diphenylphosphinomethyl)-2,2-dimethyl-1,3-dioxalane (Scheme 1), which was first prepared by Dang and Kagan [1], is an important bidentate ligand. It has been extensively used in transition metal complexes for asymmetric catalytic reactions, such as asymmetric hydrogenation [2–4], hydroformylation [5,6], hydrosilylation [7], hydrocarboxylation [8] and asymmetric cross-coupling reactions [9]. *R,R*-DIOP usually acts as a bidentate chelating ligand, and a great number of transition metal complexes based on it have been reported, for instance, the complexes of rhodium [10,11], ruthenium [12–14], cobalt [15,16], nickel [17–20], palladium [17] and platinum [17,21–24] and so on. On the other hand, *R,R*-DIOP coordinated copper and cadmium complexes are sparsely reported, perhaps because of their poor catalytic properties [25]. However, copper (I)-phosphine and cadmium (II)-phosphine coordination chemistry have aroused considerable interests in past decades as they could create some interesting coordination environments and striking structures, such as binuclear [26–30], trinuclear [31,32], cubane-like [33,34], tetramer [35,36], hexanuclear cluster [37], chain structure [38,39], molecular cavity [40] and so on. Moreover, several

novel copper (I) chiral diphosphines complexes have been used to form rhodium complex catalysts for chiral hydrogenations [25]. Another binuclear copper (I) phosphine complexes are used for photocatalytic reductions of the 4,4'-dimethyl-2,2'-bipyridinium ion in alcohols [41]. In addition, some trinuclear cadmium (II) phosphide complexes have been tested to be potential precursors to electronic materials [32]. In this paper, we describe the syntheses, crystal structures of a binuclear complex [CuCl(*R,R*-DIOP)]₂ (**1**) and a helical polymer [CdCl₂(*R,R*-DIOP)]_n (**2**) (Schemes 2 and 3), along with their UV–vis and fluorescence spectra.

2. Experimental

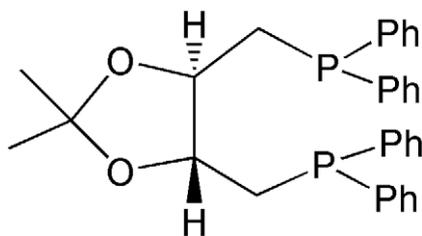
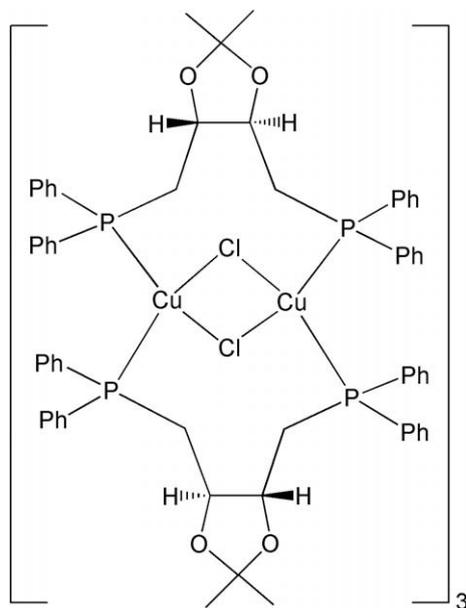
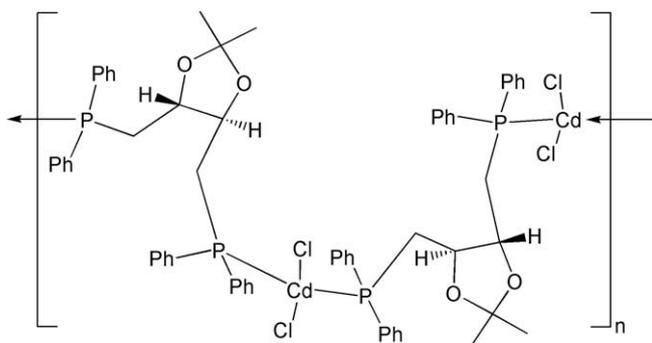
All reactions and manipulations were carried out under dry argon with standard vacuum line techniques. Solvents were purified, dried, deoxygenated and distilled before use. Metal salts were of reagent grade and used as received without further purification.

2.1. Synthesis of complex (1)

A solution of CuCl (0.05 mmol, 0.005 g) in anhydrous ethanol (10 ml) was injected dropwise into a solution of *R,R*-DIOP (0.05 mmol, 0.025 g) in CH₂Cl₂ (15 ml) under argon. Then the resulting mixture was stirred at 343 K for 4 h. After that, the cooled

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Scheme 1. *R,R*-DIOP.Scheme 2. Schematic representation of **1**.Scheme 3. Schematic representation of **2**.

reaction mixture was filtered to remove traces of CuCl. Four days later, colourless block shaped crystals suitable for X-ray diffraction were grown from the filtrate by slow evaporation. Yield: 7.0 mg (47%). Anal. Calcd for $C_{62}H_{64}Cl_2Cu_2O_4P_4$ (%): C, 62.26; H, 5.35. Found: C, 62.21; H, 5.43. IR (cm^{-1}): 3049.1 ($\nu(C=C-H)$), 2989.3 ($\nu(CH)$), 2929.4, 2854.2 ($\nu(CH_2)$), 1634.7, 1616.5 ($\nu(C_6H_6)$, skeleton), 1383.7, 1368.2 ($\delta(CH_3)_2CH$), 1099.2 ($\nu(C-O)$), 786.8 [$\gamma(C=C-H)$], 738.8 ($\gamma(CH_2)$).

2.2. Synthesis of complex (2)

A solution of $CdCl_2 \cdot 2.5H_2O$ (0.025 mmol, 0.0057 g) in anhydrous ethanol (10 ml) was injected dropwise into a solution of *R,R*-DIOP

(0.05 mmol, 0.025 g) in CH_2Cl_2 (15 ml) under argon. The resulting mixture was stirred at 353 K for 5 h, and then cooled to room temperature. The cooled reaction mixture was filtered and colourless claviform-shaped crystals suitable for X-ray diffraction were grown from the filtrate by slow evaporation one day later. Yield: 9.1 mg (53%). Anal. Calcd for $C_{31}H_{32}CdCl_2O_2P_2$ (%): C, 54.56; H, 4.96. Found: C, 54.68; H, 4.82. IR (cm^{-1}): 2989.7 ($\nu(C=C-H)$), 2981.5 ($\nu(CH)$), 2922.2, 2897.7 ($\nu(CH_2)$), 1585.2, 1437.1 ($\nu(C_6H_6)$, skeleton), 1386.4, 1372.8 ($\delta(CH_3)_2CH$), 1097.5 ($\nu(C-O)$), 748.9 [$\gamma(C=C-H)$], 726.3 ($\gamma(CH_2)$). Furthermore, other transition metal (II) salts MCl_2 , $M(NO_3)_2$ or $M(CH_3COO)_2$ ($M = Mn, Co, Zn$) have also been tried in our experiments in a similar way. Unfortunately, there is no crystalline material after slow evaporation.

2.3. Physical measurements

All the spectral data were collected at room temperature.

The C, H elemental analyses were performed on an Elementar Vario EL elemental analyzer. The IR spectrum was recorded on a Shimadzu IR-408 spectrophotometer using the KBr pellet in the range of 4000–400 cm^{-1} . Electronic spectra were measured on a U-3100 UV/vis spectrophotometer. An F-4500 FL Fluorescence Spectrophotometer was used to record the photoluminescence spectrum. The solid samples of **1**, **2** and free *R,R*-DIOP were locked between two glass slides and then measured.

The single-crystal X-ray diffraction data for **1** and **2** were collected on a Bruker APEX-II CCD area detector diffractometer using graphite-monochromatized Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$). Cell constants and orientation matrix for data collection were obtained from least-squares refinement by using the setting angles in the range of 2.27–25.50 for **1** and 2.34–25.50 for **2**, respectively. Absorption corrections were applied using the SADABS program [42]. The structures were solved by direct methods [43] and refined by full-matrix least squares on F^2 using the SHELXL97 software [44]. All the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. The absolute configuration of them were confirmed by values of the Flack parameter of 0.000(7) for **1** and $-0.067(16)$ for **2** [45]. Their crystallographic data are listed in Table 1, selected bond lengths (\AA) and angles ($^\circ$) are shown in Tables 2 and 3.

3. Results and discussion

3.1. Structural description of $[CuCl(R,R-DIOP)]_2$ (**1**)

Single-crystal X-ray diffraction analysis reveals that **1** is a binuclear compound. Its crystal cell is constructed from three discrete but similar binuclear molecules with no crystallographically imposed symmetry (Fig. 1). It can be seen that the structures of molecules **1a**, **1b** and **1c** are nearly the same as one another. **1a** (**1b** or **1c**) character a Cu_2 core which is quadruply bridged by all the four ligands (two chloride ions are μ_2 -bridging and two *R,R*-DIOP are bismonodentate ligands). Each Cu^I ion is four-coordinated to two P atoms and two chloride ions in a distorted tetrahedral environment (Fig. 2). **1a**, **1b** or **1c** is a double ring structure: the inner ring is comprised of the two chloride ions and two copper atoms, forming a rhombic four-membered ring Cu_2Cl_2 (the angles of $Cl-Cu-Cl$ and $Cu-Cl-Cu$ are 99.81(6) $^\circ$, 101.13(6) $^\circ$, 80.26(5) $^\circ$, 78.79(5) $^\circ$ for **1a**; 97.76(6) $^\circ$, 99.31(6) $^\circ$, 81.55(5) $^\circ$, 81.37(5) $^\circ$ for **1b**; 96.93(6) $^\circ$, 99.42(6) $^\circ$, 83.00(5) $^\circ$, 80.64(5) $^\circ$ for **1c**, respectively), with $Cu \cdots Cu$ and $Cl \cdots Cl$ as diagonals; while the outer ring consists of a $Cu-DIOP-Cu-DIOP$ 14-membered ring, in which the four C atoms (C26, C27, C57, C58 in **1a**; C88, C89, C119, C120 in **1b**; C150, C151, C181, C182 in **1c**) are chiral carbon atoms with *R* absolute

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