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Note

Copper(I) complexes of new N₂S₂ donor Schiff-base ligands derived from 1,2-bis-(2-amino-phenylsulfanyl)ethane

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ABSTRACT

A dinuclear copper(I) complex, [{Cu(PPh₃)(I)}₂((μ-L¹)] (**1**), and a one-dimensional copper(I) coordination polymer, [Cu₂(μ-I)₂(μ-L²)]ₙ (**2**), with two new Schiff base ligands, L¹ = 1,2-bis-[2-(*trans*-phenylcinnam-aldimino)-phenylsulfanyl]-ethane, L² = 1,2-bis-[2-(benzaldimino)-phenylsulfanyl]-ethane have been synthesized. The ligands L¹ and L² have been prepared by the condensation of 1,2-bis-(2-aminophenyl-sufanyl)-ethane with β-phenyl-cinnamaldehyde and benzaldehyde respectively. The ligands and their copper complexes have been characterized by elemental analyses, FT-IR, UV–Vis and ¹H NMR spectroscopy and their structures have been fully confirmed by single-crystal X-ray analysis. The two Schiff bases act as N₂S₂-bis-bidentate chelating ligands coordinating to Cu(I) centers in an anti-form. The coordination geometry around Cu(I) centers in the two complexes **1** and **2** is a distorted tetrahedron. The electrochemical properties of **1** and **2** have also been investigated by cyclic voltammetry and both copper complexes show irreversible redox behavior.

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1. Introduction

The coordination chemistry of copper(I) complexes of diimine ligands has been the focus of intensive research not only because they have diverse structures and rich photophysical and redox properties [1–4] but also because they have found important applications in bioinorganic chemistry [5,6], preparation of functional materials [7–9], and design of supramolecular assemblies [10–13]. Copper(I), with its d¹⁰ electronic configuration, is well known for forming tetrahedral coordination geometries. Through careful choice of ligand topology, copper(I) centers can be utilized for the template directed synthesis of catenanes, rotaxanes and knots [5,6].

Nowadays, efforts have been devoted to the design and synthesis of structurally flexible N/S donor ligands that can adopt various coordination modes [14,15]. The main objective is to produce new functional materials with specific molecular arrangements capable of showing the desirable properties [16,17]. With flexible ligands, the competition between chelating and bridging coordination modes is an important factor in producing mono, di, and polynuclear metal complexes [18–21]. We have recently studied the coordination behavior of several Schiff-base ligands such as ca₂en, Phca₂en, Phca₂dab, ca₂dapte and (thio)₂dapte [22–27]. While ca₂en and Phca₂en act as simple bidentate chelates [22–25], ca₂dapte and

(thio)₂dapte coordinate as bis-bidentate ligands, bridging between two metal ions [26,27]. Interestingly, the ligand ca₂dapte acts both as a bis-bidentate bridging ligand, as in [Cu₂(ca₂dapte)(PPh₃)₂X₂] complexes, with two independent bidentate moieties linked by a flexible bridge, and as a tetradentate ligand in [Cu(ca₂dapte)]ClO₄ complex wrapping around the copper center in a distorted tetrahedral fashion [26]. In the present paper, we describe the synthesis of the new Schiff-base ligands L¹ and L² (Scheme 1) and their copper(I) complexes.

2. Experimental

2.1. Materials and methods

All solvents and chemicals were purchased from commercial sources and used as received. 1,2-bis(o-aminophenylthio)ethane (dapte) was prepared as reported in [26]. Elemental analyses were performed by using a Elementar Vario EL III elemental analyzer. UV–Vis spectra were recorded on a JASCO V-570 spectrophotometer. Infrared spectra (KBr pellets) were obtained on a FT-IR JASCO 680 plus spectrophotometer. ¹H NMR spectra were measured with a Bruker AVANCE III 400 MHz spectrometer. Proton chemical shifts are reported in ppm relative to Me₄Si as internal standard. The redox properties of the complexes were studied by cyclic voltammetry. Cyclic voltammograms were recorded by using a SAMA 500 Research Analyzer. Three electrodes were utilized in this system, a glassy carbon working electrode, a platinum disk auxiliary

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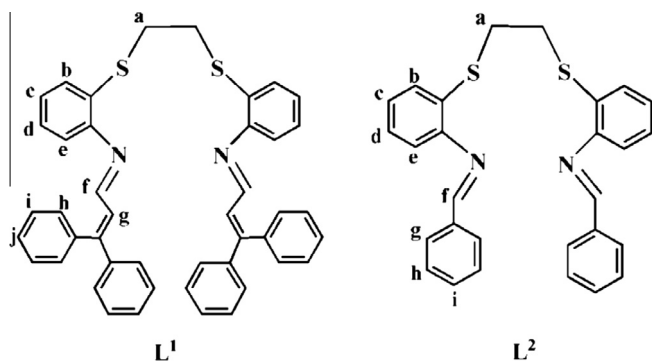
Scheme 1. Chemical formula of the Schiff base ligands.

electrode and Ag wire as reference electrode. The glassy carbon working electrode (Metrohm 6.1204.110) with 2.0 ± 0.1 mm diameter was manually cleaned with 1 μm alumina polish prior to each scan. Tetrabutylammonium hexafluorophosphate (TBAH) was used as supporting electrolyte. Cyclic voltammetric measurements were performed in DMF. The solutions were deoxygenated by purging with Ar for 5 min. All electrochemical potentials were calibrated versus internal $Fc^{+/0}$ ($E^0 = 0.46$ V versus SCE) couple under the same conditions [28].

2.2. Synthesis

2.2.1. Synthesis of L^1

A solution of phenylcinnamaldehyde (416 mg, 2 mmol) in ethanol (5 mL) was added to a stirring solution of dapte (276 mg, 1 mmol) in ethanol (20 mL). The mixture was refluxed for 6 h to give a yellow precipitate. After cooling to room temperature, the product was filtered off and washed with cold ethanol. Yield 96%; Anal. Calc. for $C_{44}H_{36}N_2S_2$: C, 80.45; H, 5.52; N, 4.26; S, 9.76. Found: C, 80.81; H, 5.34; N, 4.29; S, 9.74%. FT-IR (KBr, cm^{-1}) ν_{max}: 1607 s (C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CHCl$_3$): 362 (15230), 290 (78840). ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 3.20 (s, 4H, H$_a$), 6.75–6.77 (d of d, 2H, H$_g$), 7.08–7.45 (m, 28H, H$_{b,c,d,e,h,i,j}$), 8.03 (d, 2H, H$_f$).

2.2.2. Synthesis of L^2

The ligand L^2 was prepared by a procedure similar to that of L^1 except that benzaldehyde (212 mg, 2 mmol) was used instead of phenylcinnamaldehyde. Yield 87%. Anal. Calc. for $C_{28}H_{24}N_2S_2$: C, 74.30; H, 5.34; N, 6.19; S, 14.17. Found: C, 74.71; H, 5.28; N, 6.20; S, 14.07%. FT-IR (KBr, cm^{-1}) ν_{max}: 1623 s (C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (CHCl$_3$): 343 (16380), 291 (99270). ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 3.22 (s, 4H, H$_a$), 7.41 (dd, 2H, H$_e$), 7.50–7.69 (m, 12H, H$_{b,c,d,h,i}$), 7.94 (dd, 4H, H$_g$), 8.38 (d, 2H, H$_f$).

2.2.3. Synthesis of $[\{Cu(PPh_3)(I)\}_2((\mu-L^1)]$ (1)

To a solution of CuI (38 mg, 0.2 mmol) (52 mg, 0.2 mmol) in CH$_3$CN (5 mL) was added a solution of L^1 (66 mg, 0.1 mmol) in CH$_2$Cl$_2$ (5 mL) and the mixture was stirred at room temperature for about 10 min to give a clear dark-red solution. A solution of PPh$_3$ (52 mg, 0.2 mmol) in CH$_3$CN (5 mL) was then added. Dark-red single crystals of 1 suitable for X-ray analysis were obtained by slow evaporation of solvents. Yield 79%. Anal. Calc. for $C_{80}H_{66}N_2P_2S_2Cu_2$-I$_2$: C, 61.50; H, 4.26; N, 1.79; S, 4.10. Found: C, 61.01; H, 4.19; N, 1.77; S, 4.06%. FT-IR (KBr, cm^{-1}) ν_{max}: 1590 s (C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (DMF): 359 (49690), 289 (62240). ^{1}H NMR (DMSO, 400 MHz): δ = 3.08 (s, 4H, H$_a$), 7.06 (br d, 2H, H$_g$), 7.13–7.53 (m, 58H, H$_{b,c,d,e,h,i,j, PPh3}$), 8.1 (d, 2H, H$_f$).

2.2.4. Synthesis of $[Cu_2(\mu-I)_2((\mu-L^2)]_n$ (2)

To a solution of CuI (38 mg, 0.2 mmol) in CH$_3$CN (5 mL) was added, with continuous stirring, L^2 (45 mg, 0.1 mmol) in CH$_2$Cl$_2$ (2 mL). The mixture was stirred at room temperature for about 10 min to give a clear orange solution. Orange single crystals of 2 suitable for X-ray diffraction were obtained by slow evaporation for several days in the form of the solvate $[Cu_2(\mu-I)_2((\mu-L^2)]\cdot CH_2Cl_2$, (2·CH$_2Cl_2$). Yield 81%. Anal. Calc. for $C_{28}H_{24}Cu_2I_2N_2S_2\cdot CH_2Cl_2$: C, 40.35; H, 2.90; N, 3.36; S, 7.69. Found: C, 40.22; H, 2.83; N, 3.34; S, 7.62%.FT-IR (KBr, cm^{-1}) ν_{max}: 1600 s (C=N). UV–Vis: λ_{max} (nm) (ε, L mol^{-1} cm^{-1}) (DMF) 342 (6970), 288(32640). ^{1}H NMR (DMSO, 400 MHz): δ = 3.14 (s, 4H, H$_a$), 7.32 (dd, 2H, H$_e$), 7.34–7.68 (m, 12H, H$_{b,c,d,h,i}$), 8.11 (d, 4H, H$_g$), 8.73 (s, 2H, H$_f$).

2.3. Crystal structure determination

Dark-red and orange crystals of 1 and 2 suitable for X-ray crystallography were obtained by slow evaporation of proper solutions of the complexes at room temperature. Single crystal X-ray diffraction data were collected at 100 K with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) utilizing a Bruker Kappa APEX-II CCD diffractometer. Data were processed with programs SAINT and SADABS for 1 and 2 [29]. The crystal structures were solved with direct methods and program SHELXL97, and were refined on F^2 with program SHELXL97 [30]. All non-H atoms were refined anisotropically. The H atoms were constrained to idealized geometries and were refined isotropically. Complex 2 contained a CH$_2$Cl$_2$ solvent molecule orientation disordered about a centre of inversion. Crystal data, together with other relevant information on structure determination, are listed in Table 1. Structural graphics was generated with program MERCURY [31].

3. Results and discussion

3.1. Synthetic study

The new tetradentate N_2S_2 donor Schiff-base ligands L^1 and L^2 were prepared by the condensation of the corresponding aldehydes with dapte in 2:1 M ratio in ethanol. The products precipitated as microcrystalline powders and were readily isolated in high yield. The ligands were characterized by CHN analysis and different spectroscopic methods.

Complex 1 was synthesized by the reaction of CuI, L^1, and PPh$_3$ in acetonitrile in 2:1:2 M ratio. Complex 2 was synthesized by the reaction of CuI with L^2 in acetonitrile solution in 1:1 M ratio (Scheme 2). Dark-red and orange crystals of these complexes were obtained in good yield, (79%) for 1 and (81%) for 2. These complexes are stable in air in the solid state.

3.2. Spectral characterization

Apart from the bands corresponding to the aliphatic and aromatic C-H stretching vibrations, the IR spectra of the free ligands L^1 and L^2 exhibit the characteristic band of the imine group, which appears at 1607 and 1622 cm^{-1} respectively. These bands are shifted to lower frequencies in the IR spectra of the corresponding complexes due to the back bonding from copper(I) center to the coordinated azomethine π^* orbital [32], and appear at 1590 cm^{-1} in 1 and 1600 cm^{-1} in 2.

The UV–Vis spectrum of L^1 in chloroform exhibits absorption bands at 290 nm ($\varepsilon = 78840$ L mol^{-1} cm^{-1} $\pi \to \pi^*$) and at 362 nm ($\varepsilon = 15230$ L mol^{-1} cm^{-1}, $n \to \pi^*$). The electronic absorption spectrum of L^2 in chloroform exhibits absorption bands at 291 nm ($\varepsilon = 99270$ L mol^{-1} cm^{-1} $\pi \to \pi^*$) and at 343 nm ($\varepsilon = 16380$ L mol^{-1} cm^{-1}, $n \to \pi^*$). It is well known that copper(I)