

Fluorenyl-Schiff-base ligands and their dicopper(II) complexes. Synthesis, structural and spectroscopic characterization and DNA binding assays

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ABSTRACT

Schiff-base ligands L1 and L2 containing fluorene as fluorophore were synthesized through condensation of salicylaldehyde and 2,6-diformyl 4-methylphenol with 6-(9-fluorenyl)-1,4,8,11-tetraazaundecane-5,7-dione, respectively. A comprehensive spectroscopic analysis was performed by elemental analysis, ESI-MS, ¹H and ¹³C NMR, FTIR, EPR, UV-Vis and emission spectroscopies. Ligand L1 binds copper(II) to form [Cu₂(L1)₂].2H₂O that crystallizes in orthorhombic system and space group *P*₂₁/*n*. Assignments to the UV-Vis and EPR spectra allowed access to Jahn-Teller stabilization energies (*E*_{JT}) at 6345 and 5435 cm⁻¹ for complexes [Cu₂(L1)₂].2H₂O and [Cu₂(L2)](ClO₄)₄.4H₂O, respectively, and to their corresponding spin orbit coupling constants $\lambda = -428$ and -398 cm⁻¹. The EPR spectrum of [Cu₂(L2)](ClO₄)₄.4H₂O in the solid state showed a half-field $\Delta m_S = \pm 2$ transition, supporting the dicopper composition. The fluorenyl copper(II) derivatives demonstrated a moderate binding to ct-DNA than the fluorenyl-ligand molecule following the increasing order of (*K*_b): L1 < [Cu₂(L1)₂].2H₂O < [Cu₂(L2)](ClO₄)₄.4H₂O.

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1. Introduction

Copper is an essential element, but it is also a pollutant and can be toxic when in high concentrations in the environment [1]. Copper concentration in the environment varies and comes from natural occurrence, mining and industrial activity. Literature presents several fluorescent sensors for copper ion, with varying degrees of sensitivity, selectivity and difficulty of preparation [2–19].

Condensation of 2,6-diformyl-4-methylphenol and diamines produces Robson-type ligands that have been investigated over the years because their coordination compounds show interesting magnetic, redox and structural properties [20–25].

Continuing our general interest in the synthesis of metal complexes of polyfunctional ligands we have recently reported the structural, magnetic and spectroscopic properties of a *bis*(semicarbazone) series prepared by Schiff condensation of 2,6-diformyl 4-

methylphenol with semicarbazide hydrochloride in 1:2 M ratio [21].

In this work we report on the preparation, characterization and properties of two coordination compounds that contain luminescent ligands (Scheme 1). Ligands **1** and **2** were prepared by connecting a diamidodiamine (6-(9-fluorenyl)-1,4,8,11-tetraazaundecane-5,7-dione) to two equivalents of salicylaldehyde and 2,6-diformyl-4-methylphenol, respectively. Both ligands contain fluorene, which is a fluorophore with recognized photophysical properties [26–30]. Despite of its binding ability, few papers on appending fluorescent groups to the diamidodiamine unit have been reported [26–33]. Also, DNA-binding assays were conducted to better investigate the interaction type of this biomolecule.

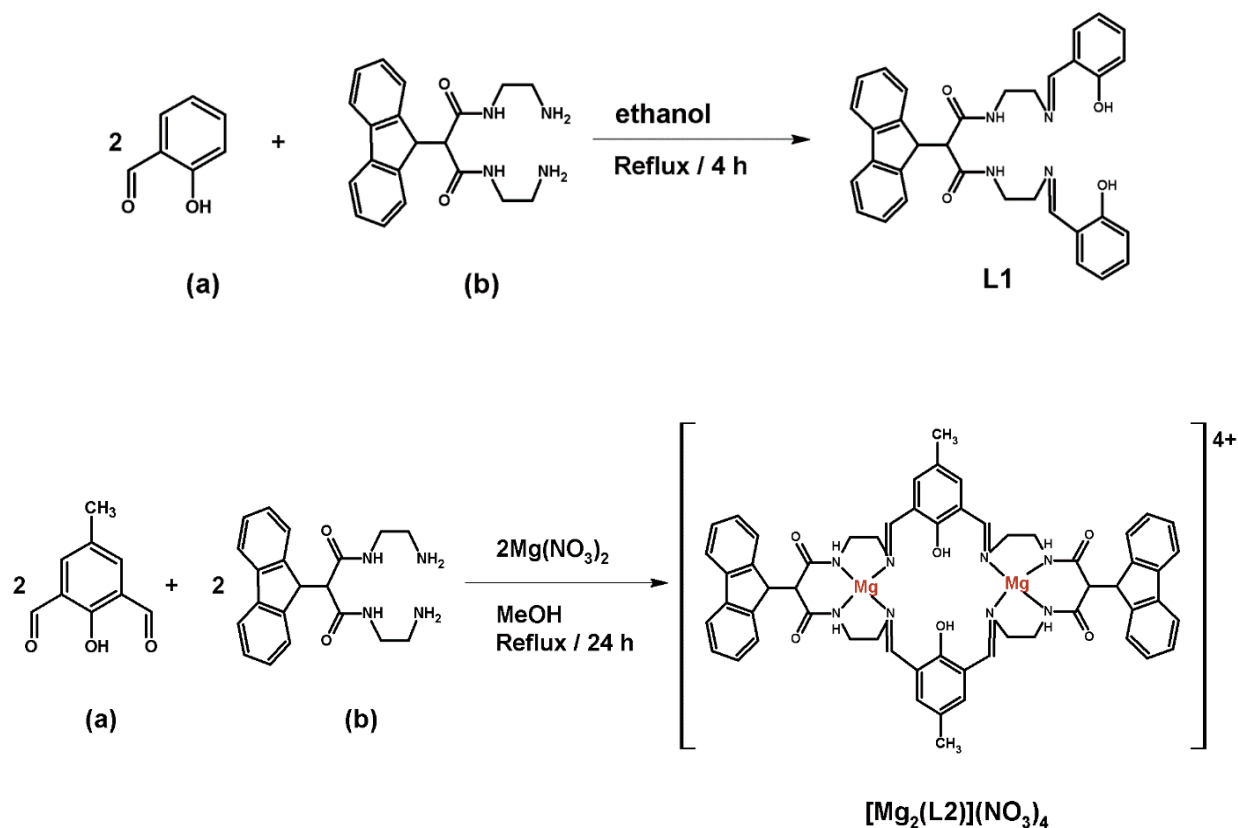
2. Experimental

2.1. Preparations

The chemicals used in this work were purchased from Sigma-Aldrich and used as supplied. 6-(9-Fluorenyl)-1,4,8,11-

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Scheme 1. Synthesis of L1 (top) and $[\text{Mg}_2(\text{L}2)](\text{NO}_3)_4$ (bottom).

tetraazaundecano-5,7-dione and 2,6-diformyl-4-methyl-phenol were prepared as described elsewhere [26,34].

Ligand **L1** (Scheme 1) and $[\text{Cu}_2(\text{L}1)_2] \cdot 2\text{H}_2\text{O}$ were synthesized according to Luo et al. [35]. Elemental analysis calculated (found) for L1, $\text{C}_{34}\text{H}_{32}\text{N}_4\text{O}_4$, $560.64 \text{ g mol}^{-1}$: C% 72.85 (72.84); H% 5.66 (5.75); N% 10.26 (10.00). ^1H NMR (δ in ppm): 7.83, d, H1; 7.88, t, H2; 7.19, t, H3; 7.41, d, H4; 4.66, d, H5; 2.85, d, H6; 3.49–3.67, m, H8 and H9; 8.39, s, H10; 6.86, m, H11 and H12; 7.32, m, H13, H14 and H15. ESI-MS (negative mode) at m/z : Calculated (observed) for $[\text{L}1-\text{H}]^-$: 559.63 (559.53). Yield for $[\text{Cu}_2(\text{L}1)_2] \cdot 2\text{H}_2\text{O}$ was 0.071 g, 28%. Elemental analysis calculated (found) for $\text{C}_{68}\text{H}_{64}\text{N}_8\text{O}_{10}\text{Cu}_2$, 1280 g mol^{-1} : C% 63.99 (63.79); H% 4.74 (4.64); N% 9.00 (8.78).

Ligand **L2** was prepared by template method. $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.00 g, 3.9 mmol) and 0.69 g (1.95 mmol) 6-(9-fluorenyl)-1,4,8,11-tetraazaundecano-5,7-dione were dissolved in 30 mL of methanol and mixed with a solution of 0.32 g (1.95 mmol) of 2,6-diformyl-4-methylformol in 10 mL of methanol. The system was kept under reflux for 24 h, resulting in an orange solution. One third of the volume was removed under vacuum and 20 mL of diethyl ether was added. The orange product was collected by filtration, washed with ether and dried under vacuum. Yield was 0.73 g (30%). Elemental analysis calculated (found) for $\text{C}_{58}\text{H}_{56}\text{Mg}_2\text{N}_{12}\text{O}_{18}$, $1257, 75 \text{ g mol}^{-1}$: C% 55.54 (55.48); H% 4.42 (4.33); N% 13.17 (13.39). ^1H NMR (δ in ppm): 7.19–8.53, m, H1; 4.65, d, H2; 3.31–3.35, m, H4; 3.01, d, H3; 2.77–2.85, m, H5; 2.15–2.35, m, H6. ESI-MS (positive mode) at m/z : Calculated (observed) for $[\text{L}2+\text{H}]^+$: 961.44(961.44).

2.1.1. $[\text{Cu}_2(\text{L}2)](\text{ClO}_4)_4 \cdot 4\text{H}_2\text{O}$

Copper perchlorate hexahydrate (0.088 g, 0.24 mmol) dissolved in 3 mL of methanol was mixed to $[\text{Mg}_2(\text{L}2)](\text{NO}_3)_4$ (0.300 g, 0.24

mmol) in 3 mL of methanol. After reflux for 2 h, the pH was set to 9 using triethylamine, and reflux was maintained for two more hours. After filtration, 2/3 of the volume was removed, leading to a brown powder, which was collected, washed with cold ethanol and dried under vacuum. Yield was 0.328 g, 88%. Elemental analysis calculated (found) for $\text{C}_{58}\text{H}_{60}\text{N}_8\text{O}_{26}\text{Cl}_4\text{Cu}_2$, 1558 g mol^{-1} : C% 44.35 (44.83); H% 4.06 (4.14); N% 7.46 (7.21).

2.2. Apparatus

Elemental analyses were done in a Perkin-Elmer 2400 analyzer. Mass spectra were measured in a high resolution ESI-MS on a microTOF QII mass spectrometer (Bruker Daltonics, Billerica, MA) from dimethylsulfoxide solutions. ^1H and ^{13}C NMR spectra were recorded in a Bruker Avance HD spectrometer at 400 MHz, DMSO was used as solvent and TMS as the internal reference. The chemical shifts are expressed in δ (ppm).

Electronic spectra in the UV–Vis range (190–820 nm) were obtained on a diode array Hewlett–Packard 8452A or Varian Cary 50 spectrophotometer in dimethylsulfoxide solutions using a 1.0 cm path length quartz cell.

Fluorescence measurements and fluorescence quantum yields were recorded in a 1.0 cm optical path length of a quartz cuvette using a Varian Cary Eclipse or Shimadzu RF5301-PC spectrofluorimeter with a concentration of $1 \times 10^{-5} \text{ mol L}^{-1}$ to minimize the re-absorption. The equipment was set at 1.5 nm slit width and 600 nm min^{-1} scan rate for both excitation and emission spectra. The solutions were always purged with nitrogen prior to the measurements to avoid quenching by dioxygen molecules. Re-absorption of the fluorescence was minimized using absorbance values smaller than 0.100 for a standard 1.0 cm optical path length quartz cuvette.

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