Research Paper

Journal of Chemical Research

Synthesis and characterization of novel coumarin-based terpyridine ligands and their Zn(II) complexes

Journal of Chemical Research 1–6 © The Author(s) 2020 Article reuse guidelines: sagepub.com/journals-permissions DOI: 10.1177/1747519820918491 journals.sagepub.com/home/chl

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Abstract

Two novel mononuclear Zn(II) complexes, $[ZnL^1Cl_2]$ (I) $(L^1=(E)-3-(4-(2,2':6',2''-tripyridyl)-4'-styryl)-7$ diethylaminocoumarin) and $[ZnL^2Cl_2]$ (2) $(L^2=3-(4-(2,2':6',2''-tripyridyl)-4'-phenylimine)-7-diethylaminocoumarin),$ $were obtained by the solvothermal method from <math>ZnCl_2$ and coumarin-based terpyridine ligands. The complexes were characterized by spectroscopic methods and single-crystal X-ray diffraction. The Zn^{2+} in the complexes is coordinated by three nitrogen atoms of the terpyridine ligand and two chloride anions, forming a distorted trigonal bipyramidal environment. Moreover, the UV–Vis absorption and emission spectra of the ligands and complexes in diluted dichloromethane solutions were measured.

Keywords

absorption, coumarin, fluorescence, terpyridine, Zn(II) complexes

Date received: 8 February 2020; accepted: 21 March 2020



Introduction

With three nitrogen coordination sites, terpyridines have attracted widespread attention because of their excellent complexing properties as N-donor ligands toward a wide range of transition and rare earth metal ions.¹ The terpyridine-based complexes play a prominent role in research owing to their interesting and diverse properties. They have been investigated for their potential applications in materials research, polymer science, nanotechnology, catalysis, medicine, and light-to-energy conversion.^{2–8}

Among the various terpyridine ligands, a few coumarincontained terpyridines and/or their complexes have been reported to exhibit prominent properties and are used as fluorescent chemosensors or molecular energy transfer switch.^{9–11} In recent years, we have been engaging in the synthesis of novel coumarin derivatives and investigation of their fluorescent properties.^{12–15} As a part of the foregoing research in our group, we present herein the concise and efficient synthesis of two novel coumarin-based terpyridine derivatives, 3-(4-(2,2':6',2''-tripyridyl-4'-)styryl)-7-diethylaminocoumarin (L¹) and <math>3-(4-(2,2':6',2''-tripyridyl-4'-)phenylimine)-7-diethylaminocoumarin (L²). By using the above ligands, two corresponding Zn(II) complexes were obtained and characterized by infrared (IR) spectroscopy, elemental analysis, and structurally analyzed by X-ray single-crystal diffraction. Moreover, the absorption and emission spectra of the synthesized ligands and complexes in dichloromethane were measured.

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Scheme I. Synthesis routes of L¹ and L².

Results and discussion

Synthesis of ligands L^1 and L^2

The synthesis of the two ligands L^1 and L^2 is outlined in Scheme 1. The 3-formylcoumarin 3 was obtained by Vilsmeier-Haack reaction of 7-(diethylamino)coumarin with DMF (dimethylformamide) and POCl₂ as we have reported previously.¹² The compound 4 was synthesized from 2-acetylpyridine and 4-methylbenzaldehyde in three steps following the processes reported in the literature.¹⁶ Compound 3 underwent the Wittig reaction with 4 promoted by cesium fluoride in toluene under reflux condition to afford the desired ligand L1. Moreover, the 3-aminocoumarin 5 was obtained by reduction of the corresponding 3-nitrocoumarin using SnCl₂ as reductant.¹⁷ The terpyridinylbenzaldehyde 6 was also prepared from 2-acetylpyridine and 4-methylbenzaldehyde in two steps by the published procedures.¹⁸ The aminocoumarin 5 condensed with 6 in ethanol under reflux condition to provide the desired ligand L^2 in good yield.

Crystal structures of complexes | and 2

The single-crystal structures of complexes 1 and 2 are shown in Figures 1 and 2. Crystallographic data, data collection, and structure refinement details of complexes 1 and 2 are summarized in Table 1. Selected bond lengths and



Figure 1. Molecular structure of complex **I** with 30% probability displacement ellipsoids.



Figure 2. Molecular structure of complex **2** with 30% probability displacement ellipsoids.

angles are given in Table 2. Both 1 and 2 are mononuclear complexes. Complex 1 crystallizes in the C2/c space group

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Table I. Cr	ystal data and	d structure	refinement fo	or complexes	I and 2.
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Complex	I	2	
Empirical formula	$C_{14}H_{10}CI_{2}N_{4}O_{2}Zn$	C ₃₅ H ₃₉ Cl ₃ N ₅ O ₃ Zn	
Formula weight	689.91	687.90	
Crystal system	Monoclinic	Monoclinic	
Space group	C2/c	l2/c	
a (Å)	38.515(5)	17.836(5)	
b (Å)	9.919(7)	9.766(4)	
c (Å)	18.035(15)	39.474(2)	
α (°)	90	90	
β (°)	102.274(9)	102.728(3)	
γ (°)	90	90	
V (Å ³)	6732.8(11)	6706.6(5)	
Z	8	8	
D_{cole} (g cm ⁻³)	1.355	1.363	
$\mu (\text{mm}^{-1})$	0.926	2.792	
Crystal size (mm)	0.21×0.15×0.14	0.21×0.17×0.14	
Color/shape	Yellow/block	Dark brown/block	
Temperature (K)	276(1)	293(2)	
Theta range for collection	3.398-26.015	4.671-69.829	
Reflections collected	13,477	24,209	
Independent reflections	6618 (R(int) = 0.0890)	6262 (R(int) = 0.0635)	
Data/restraints/parameters	6618/0/408	6262/4/408	
Goodness of fit on F^2	0.988	1.038	
Final R indices ($l > 2\sigma(l)$)	$R_1 = 0.0783, wR_2 = 0.1373$	$R_1 = 0.0522, wR_2 = 0.1365$	
R indices (all data)	$R_1 = 0.1889, wR_2 = 0.1970$	$R_1 = 0.0724, wR_2 = 0.1569$	
Largest diff. peak and hole (e $Å^{-3}$)	0.49 and -0.40	0.39 and -0.40	

Table 2. Selected bond lengths (Å) and bond angles (°) for complexes I and 2.

Complex I								
ZnI-CII	2.266(2)	Zn I–Cl2	2.258(2)	Zn1–N1	2.210(5)			
Zn I–N2	2.103(5)	ZnI–N3	2.196(5)					
CII-ZnI-Cl2	115.64(7)	CII-ZnI-NI	96.36(15)	CII-ZnI-N2	121.76(16)			
CII-ZnI-N3	101.11(15)	Cl2–Zn1–N1	101.17(16)	Cl2–ZnI–N2	122.60(16)			
Cl2–Zn1–N3	94.61(16)	NI-ZnI-N2	74.3(2)	NI-ZnI-N3	148.5(2)			
N2-ZnI-N3	74.2(2)							
Complex 2								
ZnI-CII	2.2657(13)	Zn I–Cl2	2.2679(13)	Zn1–N1	2.183(3)			
ZnI–N2	2.105(3)	ZnI–N3	2.220(3)					
CII-ZnI-Cl2	115.71(4)	CII-ZnI-NI	99.59(9)	CII-ZnI-N2	119.65(8)			
CII-ZnI-N3	97.70(8)	Cl2–ZnI–NI	96.23(9)	Cl2–Zn1–N2	124.64(8)			
Cl2–Zn1–N3	99.98(9)	NI-ZnI-N2	74.33(11)	NI-ZnI-N3	148.23(11)			
N2-ZnI-N3	73.97(11)							

of the monoclinic system and complex 2 crystallizes in the monoclinic I2/c space group. As per the reported ZnX_2 (X=Cl, Br, I) terpyridine complexes in literature,^{19–21} Zn²⁺ ion in complex 1 (or 2) is five coordinated by three N atoms from the terpyridine ligand and two chloride anions to form a distorted trigonal bipyramidal configuration, whereby atoms N1 and N3 occupy the axial positions and atoms N2, Cl1, and Cl2 lie in the equatorial plane. Investigation of the structures reveals that the Zn–N and Zn–Cl bond lengths in complexes 1 and 2 are comparable with each other. The average Zn–N bond length is 2.170 Å for complex 1 and 2.169 Å for complex 2 in the range of 2.103–2.210 Å (1)

and 2.105–2.220 Å (2) and that of Zn–Cl is 2.262 Å for 1 and 2.266 Å for 2, respectively. All of the coordinate bond lengths are comparable with those reported in the literature.^{19–21}

In complex 1, the dihedral angles between the central pyridine motif and two outer pyridine rings are 3.68° and 11.15°, respectively. Due to steric hindrance effect, the bridged benzene ring (C16–C21) is not coplanar with the central pyridine ring, and the dihedral angle between them is 24.44°. The bond angles of C24– C23–C22 and C23–C22–C19 are 127.95° and 125.42°, respectively.



Figure 3. Absorption spectra of L^1 and complex 1 in dichloromethane $(1 \times 10^{-5} \text{ mol } L^{-1})$.



Figure 4. Absorption spectra of L^2 and complex 2 in dichloromethane $(1 \times 10^{-5} \text{ mol } L^{-1})$.

In complex **2**, the dihedral angles between the central pyridine ring and two outer pyridine rings are 2.57° and 9.51° , respectively. Also due to steric hindrance effect, the bridged benzene ring (C16–C21) is not coplanar with the central pyridine ring, and the dihedral angle between them is 23.46°. The bond angles of C23–N4–C22 and N4–C22–C19 are 117.78° and 121.99°, respectively.

Absorption and fluorescence spectra of the ligands and the Zn(II) complexes

The UV–Vis absorption spectra of the free ligands (L¹ and L²) and the corresponding complexes (**1** and **2**) in diluted dichloromethane solutions are shown in Figures 3 and 4, respectively. The absorption spectrum of the ligand L¹ shows absorptions at 253, 277, and 436 nm, while the absorption peaks are observed at 284, 320, and 451 nm in the absorption spectrum of the complex **1**. The absorption peak at 451 nm of complex **1** is assigned to the M \rightarrow L charge-transfer transition, which indicates that there are strong coordination bonds between the ligand L¹ and the Zn(II) ions.²² The spectral shape of the complex **1** is similar to that of the ligand L¹. Compared with the free ligand L¹, the absorption peaks of the zinc complex **1** are bathochromically shifted.

As shown in Figure 4, the ligand L^2 shows three absorption peaks at 251, 288, and 442 nm. Compared with the



Figure 5. Emission spectra of L^1 and complex I in dichloromethane $(I \times 10^{-5} \text{ mol } L^{-1})$.



Figure 6. Emission spectra of L^2 and complex **2** in dichloromethane $(I \times I0^{-5} \text{ mol } L^{-1})$.

absorption peaks of the free ligand, the absorptions at 251 and 288 nm are blue-shifted to 241 and 286 nm, while the absorption at 442 nm is red-shifted to 451 nm in the absorption spectrum of complex **2**. The absorption peak at 451 nm of complex **2** is also assigned to the $M \rightarrow L$ charge-transfer transition.²²

The fluorescence emission spectra of the dilute dichloromethane solutions of the L¹, complex 1 and L², complex 2 are shown in Figures 5 and 6, respectively. The ligands L¹ and L² exhibit emissions at 511 and 513 nm upon excitation at 436 and 396 nm, respectively. The green emissions of L¹ and L² should be assigned to the intra-ligand π - π * transition.²³ Compared with the free ligands L¹ and L², complexes 1 and 2 show fluorescence emissions at 562 and 547 nm, respectively. The maximum emission wavelengths of complexes 1 and 2 are significantly red shifted from those of the free ligands which are mainly originated from the coordination of the metal to the ligands,²⁴ resulting in increasing the electron absorption abilities of the ligands and decreasing the energy of the excited states.

Conclusion

In summary, two novel coumarin-based terpyridine ligands and their corresponding mononuclear Zn(II) complexes have been synthesized and characterized by

spectroscopic methods and single-crystal X-ray diffraction. In the two complexes, Zn^2 + is five coordinated with three nitrogen atoms from the terpyridine skeleton and two chloride atoms, resulting in the Zn atom being located at the distorted trigonal bipyramidal center. The fluorescence emissions of the complexes are significantly red shifted from those of the corresponding ligands mainly due to the coordination of the metal with the ligands. Applicability of these coumarin-based terpyridine ligands and their Zn(II) complexes is yet to be established.

Experimental

Materials and general methods

All chemicals and solvents were analytical reagent grade, commercially available and used without further purification. Elemental analyses (C, H and N) were performed on a GmbH VariuoEL V3.00 automatic elemental analyzer. ¹H NMR and ¹³C NMR spectra were recorded using a Bruker Avance DRX-400 MHz or a Bruker Avance III 500 MHz spectrometer. Melting points were determined by a microscope apparatus and are uncorrected. IR spectra were recorded on a Digilab FTS-3000 FTIR spectrophotometer. UV–Vis absorption and fluorescence spectra were recorded on a Hitachi U-3900H spectrometer and on a Hitachi F7000 FL spectrophotometer, respectively. X-ray single-crystal diffraction measurements were made on a Bruker X8 APEX diffractometer working with graphite monochromated Mo Kα radiation.

Synthesis of L^{I}

A mixture of compound 3 (0.74 g, 3.0 mmol), compound 4 (2.99 g, 4.5 mmol), and cesium fluoride (0.82 g, 5.4 mmol)in anhydrous toluene (50 mL) was refluxed for 11 h. After completion, the reaction mixture was cooled to room temperature and filtrated. The organic phase was washed with water $(3 \times 50 \text{ mL})$, dried over Na₂SO₄, and evaporated under vacuum. The resulting residue was purified by column chromatography over silica gel using petroleum ether/ ethyl acetate/dichloromethane (v/v/v=3:1:1) as eluent to afford L^1 as orange solid. Yield 0.49 g (30%), m.p. 242– 243 °C. Anal. calcd for C₃₆H₃₀N₄O₂: C, 78.52; H, 5.49; N, 10.17; found: C, 78.43; H, 5.37; N, 10.12%. IR (KBr, cm⁻¹): 1706, 1619, 1579, 1343, 1182, 1119, 786, 751. ¹H NMR (400 MHz, CDCl₂): δ 8.76–8.74 (m, 4H), 8.67 (d, J=7.6 Hz, 2H), 7.92–7.86 (m, 4H), 7.70–47.6 (m, 3H), 7.53 (d, J=16.4 Hz, 1H), 7.37–7.28 (m, 3H), 7.17 (d, J=16.4 Hz, 1H), 6.59 (d, J=8.8 Hz, 1H), 6.51 (s, 1H), 3.42 (q, J=7.2 Hz, 4H), 1.22 (t, J=7.2 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 161.36, 156.28, 155.92, 155.65, 150.50, 149.62, 149.12, 138.50, 137.24, 136.80, 129.31, 128.86, 127.51, 127.05, 124.01, 123.77, 121.32, 118.46, 117.59, 109.12, 109.09, 97.17, 44.86, 12.49.

Synthesis of L²

Compound 5 (0.69 g, 3.0 mmol) and compound 6 (1.01 g, 3.0 mmol) were dissolved in ethanol (30 mL). The

mixture was heated at 70 °C for 9h. After completion, the reaction mixture was cooled to room temperature. The solid was filtered, washed with ethanol, and dried at room temperature to afford L² as orange solid. Yield 1.47 g (89%). m.p. 242–244 °C. Anal. calcd for C₃₅H₂₉N₅O₂: C, 76.21; H, 5.30; N, 12.70; found: C, 76.15; H, 5.41; N, 12.62%. IR (KBr, cm⁻¹): 1708, 1624, 1584, 1404, 1256, 1125, 787, 736. ¹H NMR (500 MHz, CDCl₃): δ 9.50 (s, 1H), 8.79-8.74 (m, 4H), 8.68 (d, J=7.5 Hz, 2H), 8.05 (d, J=8.5 Hz, 2H), 8.01 (d, J=8.5 Hz, 2H), 7.91–7.87 (m, 2H), 7.73 (s, 1H), 7.38–7.34 (m, 3H), 6.62 (dd, J=8.5 and 2.0 Hz, 1H), 6.55 (d, J=2.0 Hz, 1H), 3.44 (q, J=7.0 Hz, 4H), 1.23 (t, J=7.0 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): δ 160.11, 159.12, 156.15, 156.03, 155.00, 150.54, 149.15, 140.80, 137.72, 137.47, 136.93, 129.18, 128.07, 127.61, 123.90, 121.40, 118.84, 109.33, 97.11, 44.90, 12.51.

Synthesis of complex I

Zinc(II) chloride (4.1 mg, 0.03 mmol) was dissolved in anhydrous ethanol (2 mL), L¹ (16.5 mg, 0.03 mmol) was dissolved in dichloromethane (6 mL). The two portions were mixed in a 25-mL Teflon-lined stainless steel autoclave. The autoclave was heated to 130 °C in an oven and kept there for 3 days and then allowed to cool. When the autoclave reached room temperature, yellow block crystals were obtained and used to collect the single-crystal X-ray data. Yield 41% based on ZnCl₂. IR (KBr, cm⁻¹): 1706, 1637, 1594, 1356, 1185, 1121, 799, 768, 525, 451. Anal. calcd for $C_{36}H_{30}Cl_2N_4O_2Zn$: C, 62.95; H, 4.40; N, 8.16; found: C, 62.90; H, 4.46; N, 8.13%.

Synthesis of complex 2

Zinc(II) chloride (5.4 mg, 0.04 mmol) was dissolved in anhydrous ethanol (2 mL), L² (22.0 mg, 0.04 mmol) was dissolved in trichloromethane (6 mL). The two portions were mixed in a 25-mL Teflon-lined stainless steel autoclave. The autoclave was heated to 130 °C in an oven and kept there for 3 days and then allowed to cool. When the autoclave reached room temperature, dark brown block crystals were obtained and used to collect the single-crystal X-ray data. Yield 30% based on ZnCl₂. IR (KBr, cm⁻¹): 1708, 1632, 1603, 1413, 1258, 1125, 796, 744, 518, 462. Anal. calcd for $C_{35}H_{29}Cl_2N_5O_2Zn$: C, 61.11; H, 4.25; N, 10.18; found: C, 61.15; H, 4.28; N, 10.13%.

Crystal structure determination

X-ray single-crystal diffraction data of complexes 1 and 2 were recorded using a Super Nova Dual (Cu at zero) diffractometer with a monochromated Mo K α radiation (λ =0.71073 Å). The Lp factor semi-empirical absorption corrections were applied using the SADABS program.²⁵ The structures were solved by the direct methods (SHELXS-2014).²⁶ All hydrogen atoms were added theoretically and difference-Fourier map revealed the positions of the remaining atoms. All non-hydrogen atoms were refined anisotropically using a full-matrix least-squares procedure on F^2 with SHELXL-2014.²⁶

Acknowledgements

We thank the Instrument Analysis Center of Lanzhou Jiaotong University.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) received no financial support for the research, authorship, and/or publication of this article.

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Supplemental material

Supplemental material is available online for this article.

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