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Synthesis, Crystal Structure and Characterizations of New 3,4,7,8-Tetrachloro-1,10-Phenanthroline Zn(II) Complex

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Abstract A novel 3,4,7,8-tetrachloro-1,10-phenanthroline (Cl$_4$phen) Zn(II) complex has been synthesized. The complex, [Zn(Cl$_4$phen)$_2$(H$_2$O)$_2$](NO$_3$)$_2$·CH$_3$CH$_2$OH (**1**), has been identified and characterized by single crystal X-ray diffraction, elemental analysis, FT-IR, thermogravimetric analysis and photoluminescence studies. Single crystal X-ray diffraction analysis reveals that complex (**1**) belongs to the monoclinic system, space group $P2(1)/c$, $a = 10.061(2)$ Å, $b = 18.924(4)$ Å, $c = 18.189(4)$ Å, $\beta = 100.94(3)°$, and $Z = 4$. Complex (**1**) consists of cationic species [Zn(Cl$_4$phen)$_2$(H$_2$O)$_2$]$^{2+}$, NO$_3^-$ and CH$_3$CH$_2$OH. The zinc atom displays a distorted *cis*-N$_4$O$_2$ octahedral geometry. Via extended Zn–O–H···O–N–O···H–O–Zn bridge, every mononuclear unit is linked with other ones to form one-dimensional (1D) infinite chain of hydrogen bond system. Three-dimensional (3D) polymeric network arrangement was built via weak C–H···O and π-stacking interactions between Cl$_4$phen moieties. A solvent-dependency effect of complex (**1**) was observed in spectroscopic properties.

Keywords 3,4,7,8-Tetrachloro-1,10-phenanthroline ·
Zn(II)complex · Hydrogen bonds · π-Stacking

Introduction

Due to their interesting biological activities, such as antibacterial [1], anti-convulsant [2] and antiproliferative–antitumor [3–5] activity, zinc(II) complexes had attracted great attention in the recent years. As drugs for the treatment of Alzheimer disease [6], zinc(II) complexes had been structurally characterized. Zinc(II) complexes had also showed properties of DNA binding in the very recent research [7]. Moreover, zinc(II) complexes with appropriate ligands can be applied in optical devices, such as OLED [8] and light switching device [9].

Behaving as σ(chelate) donor/π acceptor ligand, 1,10-phenanthroline with the low-lying π* orbitals is attractive to many chemists due to its tunability. Some research results indicate that the lowest-lying orbital of 1,10-phenanthroline depends on the substituent pattern of 1,10-phenanthroline [10, 11]. Several efforts, such as increasing the conjugation systerm of 1,10-phenanthroline [12] and extending the *N*-heterocyclic aromatic ring [13], have been reported to tune the physical and chemical properties of the 1,10-Phenanthroline π system through chemical modification. Multiple acceptor effect by perchlorination of 1,10-phenanthroline makes π* orbitals of octochloro-1,10-phenanthroline strongly stabilized with 1.69 eV lower than 1,10-phenanthroline itself [14]. Tetra-chloration of 1,10-phenanthroline can also lower the of π* orbitals to bring about some different photochemical and photophysical properties. Meanwhile, 1,10-phenanthroline moiety can efficiently provide π–π stacking interactions in either intra- or inter-molecular mode. This feature contributes the stability of structures as well as the formation of extended supramolecular structures [15]. Here, we report the synthesis, crystal structure and photoluminescence properties of zinc(II) complex (**1**). Complex (**1**) consist of

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$[Zn(Cl_4phen)_2(H_2O)_2]^{2+}$ unit, one ethanol molecular and two non-coordinating nitrate radical anions in the unit cell. Adjacent units are linked by hydrogen bonds and π-stacking interactions to form three-dimensional structure.

Experimental

Materials and Physical Measurements

3,4,7,8-Tetrachloro-1,10-phenanthroline was prepared by the methods as reported earlier [16], then purified by recrystallization twice in DMF. All other chemicals were commercially available and used without further purification. Elemental analysis was performed on a Elementar Vario EL III elementer analyzer. IR spectra were obtained as KBr discs on an ABB Bomem FTLA 2000-104 spectrophotometer in the 4,000–500 cm^{-1} region. Thermal analysis (TG) measurements were performed using Mettler Toledo TGA/SDTA85/e Thermal Analyzer with heating rate of 20 °C/min. The fluorescent data were collected on a RF-5301 double beam spectrofluorometer at room temperature. The spectroscopic absorption spectra were scanned on a TU-1901 double beam ultraviolet-visible spectrophotometer. ^{1}H-NMR spectra were scanned with a Bruker AMX400 spectrometer.

Preparation of [Zn(Cl₄phen)₂(H₂O)₂](NO₃)₂·CH₃CH₂OH (1)

To an solution (20 mL) of zinc nitrate (3.0 g, 10 mmol) in ethanol was added an aqueous solution (10 mL) of 3,4,7,8-tetrachloro-1,10-phenanthroline (2.0 g, 10 mmol) in CHCl₃ with stirring. The mixture was heated to reflux and stirred for 2 h. Crystalline solid was obtained by slow evaporation of the solvent. Yield: 4.1 g, 90%. *Anal.* Calcd. for $C_{26}H_{18}Cl_8N_6O_9Zn$ (mol. wt. 907.43): C, 34.40; H, 1.98; N, 9.26. Found: C, 34.62; H, 1.90; N, 9.18. IR (cm^{-1}): 3,441(br, m), 1,611(w), 1,576(w), 1,499(w), 1,416(m), 1,384(s), 1,327(m), 1,203(w), 845(w), 824(w). ^{1}H-NMR (DMSO-d_6): δ 8.285(s, 4 H, phen-H); 8.023(d, 4 H, phen-H).

X-ray Data Collection and Structural Determination

The diffraction data is collected on a Bruker Smart AP EX II CCD diffractionmeter with graphite monochromated Mo–Ka radiation ($\lambda = 0.71073$Å) at 273 K. Absorption corrections are applied by SADABS. The structure was solved by direct methods and refined with full-matrix least-squares technique using SHELXTL 97 [17]. All nonhydrogen atoms were refined with anisotropic displacement parameters. The crystallographic details and selected bond lengths (Å) and bond angles (°) are shown in Tables 2 and 3.

Result and Discussion

^{1}H-NMR, IR Spectra and Thermal Analysis

The ^{1}H-NMR spectra show that the signals of aromatic protons in complex (**1**) shift to upper field (lower δ values), compared to the free ligand. It indicates that complex (**1**) is diamagnetic similar as the reported six-coordinated Zn(II) complex [18].

The IR spectra of the complex show a broad peak at 3,441 cm^{-1} assignable to σ(OH) stretching vibrations of ethanol molecular and coordinated water molecules [19]. The observed position of the σ (OH) bands is in agreement with the participation of water molecules and ethanol molecular in hydrogen bonds. The strong absorption band at 1,384 cm^{-1} is attributed to non-coordinated NO_3^- [20] in accordance with the result of the X-ray analysis detailed below.

The thermal gravimetric (TG) curve of (1) is shown in Fig. 1. The total weight loss of 85.12% (calculated value: 84.55%) in the range of 25–697 °C agrees with the release of two ligands, two water, ethanol and nitrate anions. The remainder of 14.88% corresponds to Zn and two Cl atoms (calculated value: 15.02%) of total weight. Decomposition of complex (**1**) starts at 97 °C. There is a weight loss of 4.6% at 121 °C corresponding to the loss of non-coordinated ethanol molecule (calcd. 5.07%). The following weight loss of 4.44% at 229 °C may attribute to the loss of two coordinated water molecules (calcd. 4.09%). With the loss of two Cl₄-phen moieties, complex (**1**) decompose slowly in the temperature range of 229–697 °C, in concomitance with the reduction of nitrate anions. The residue is in 14.88% of total weight, consistent with the weight of
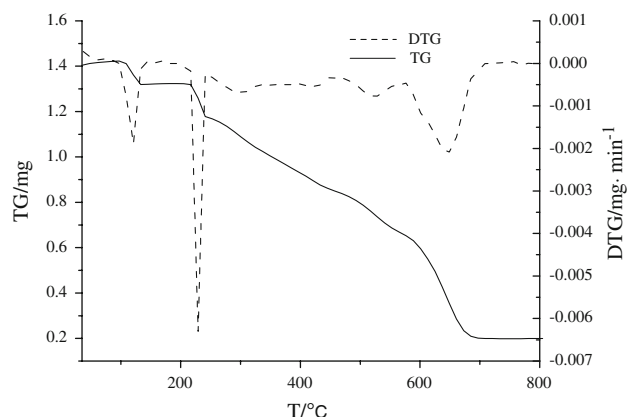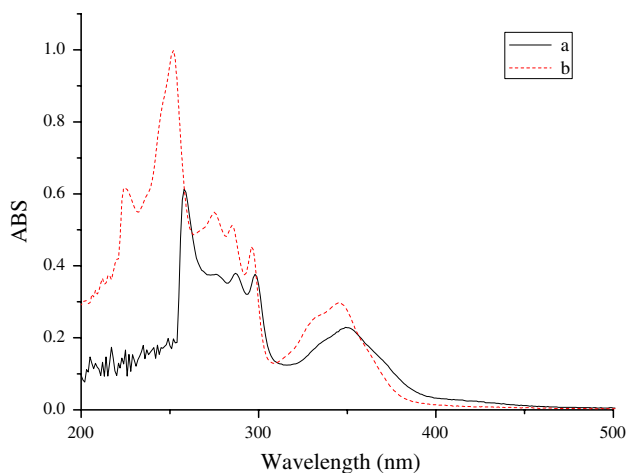

Fig. 1 TG-curve of Complex (**1**)

Zn and two Cl atoms in complex (**1**). As illustrated in Fig. 1, the complex (**1**) seems less stable than the reported [Zn(H₂O)₄(phen)](NO₃)₂·H₂O(ca.320 °C) [21].

Spectroscopic Absorption and Photoluminescence Properties

Spectroscopic absorption spectra of complex (**1**) in DMSO and Ethanol/dichloromethane (1:1) are shown in Fig. 2. The position of the electronic absorption maxima and the extinction coefficients for complex (**1**) are given in Table 1. Complex (**1**) has two absorption bands at about 250 and 350 nm, attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ electron transition, respectively.
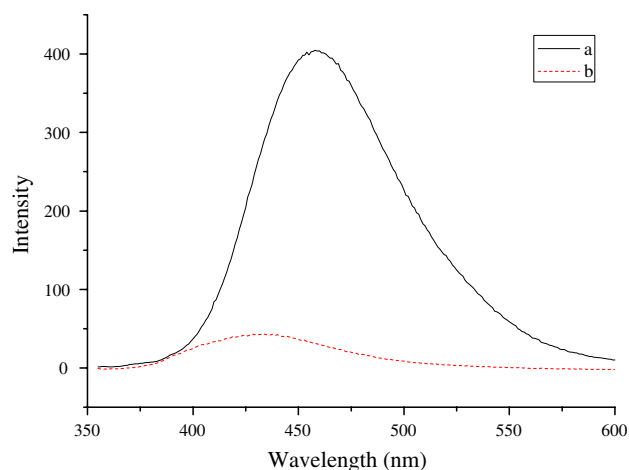
Excitation of LC (ligand center, $n \rightarrow \pi^*$) bands of complex (**1**) at room temperature produced emission at longer wavelength. The emission spectra of complex (**1**) are showed in Fig. 3 and the position bands are included in Table 1. The intensity of emission peak at 458 nm in DMSO is much stronger than that at 423 nm in Ethanol/dichloromethane (1:1). It reveals that complex (**1**) show solvent-dependency in the spectroscopic properties.

Fig. 3 Emission spectra of complex (**1**) at room temperature. 10^{-5} mol L^{-1}; **a** in DMSO; **b** in EtOH/CH₂Cl₂, 1:1

Descriptions of the Structure

Crystallographic data for the structure of complex (**1**) are listed in Table 2. The zinc complex (**1**) is illustrated in Fig. 4. The zinc center displays a distorted octahedral geometry with the major distortion, which is manifested in the chelate angle formed by the Cl₄phen ligand, i.e.

Fig. 2 Spectroscopic absorption spectra of complex (**1**). 10^{-5} mol L^{-1}; **a** in DMSO; **b** in EtOH/CH₂Cl₂, 1:1

Table 1 Spectroscopic absorption (UV–Vis) and emission data of complex (**1**)

	DMSO	EtOH/CH₂Cl₂	Assignment
λ_{max}^{abs} (nm)	258	252	LC, $\pi \rightarrow \pi^*$
	349	346	LC, $n \rightarrow \pi^*$
ε (L mol^{-1} cm^{-1})	61,300	99,900	
	22,900	29,700	
λ_{max}^{em} (nm)	458	423	

Table 2 Crystal data and structure refinement for complex (**1**)

Empirical formula	C₂₆ H₁₈ Cl₈ N₆ O₉ Zn
Formula weight	907.43
Temperature	153(2) K
Wavelength	0.71073 Å
Crystal system, space group	MONOCLINIC, $P2_1/c$
Unit cell dimensions	$a = 10.061(2)$ Å
	$b = 18.924(4)$ Å $\beta = 100.94(3)$ (°)
	$c = 18.189(4)$ Å
Volume	3,400.2 Å³
Z, Calculated density	4, 1.773 Mg/m³
Absorption coefficient	1.412 mm^{-1}
F (000)	1,816
Crystal size	0.18 × 0.16 × 0.12 mm
θ range for data collection	1.57–25.05(°)
Limiting indices	$-11 \leq h \leq 11$, $-22 \leq k \leq 22$, $-21 \leq l \leq 20$
Reflections collected/unique	32301/6010 [R(int) = 0.0317]
Completeness to $\theta = 25.05$	100.00%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8488 and 0.7851
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8487/0/433
Goodness-of-fit on F^2	1.055
Final R indices [$I > 2$sigma(I)]	$R1 = 0.0398$, $wR2 = 0.1044$
R indices (all data)	$R1 = 0.0530$, $wR2 = 0.1142$
Largest diff. peak and hole	0.748 and -0.526 e Å^{-3}

Fig. 4 Diagram showing the local coordination environment around the Zn(II) atom with thermal ellipsoids drawn at the 30% probability and hydrogen atoms omitted for clarity
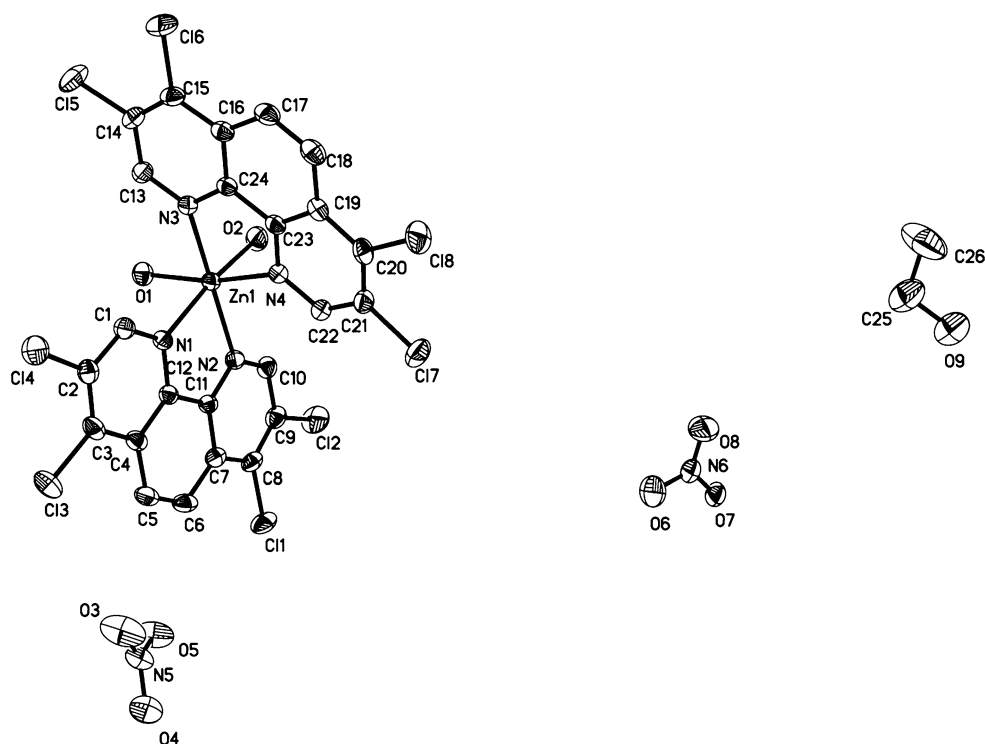
76.92(1)°. The conformation about the zinc atom is described as *sy-cis*-configuration. Selected bond distances and angles are summarized in Table 3. The average bond length of Zn–N is comparable to some other six-coordinate zinc complexes, e.g. $[Zn(phen)_2(H_2O)_2]^{2+}$ (2.17(1) Å)[22] and $[Zn(H_2O)_4(phen)]^{2+}$ (2.113(3) Å, 2.127(3) Å) [23]. The bond angles of N(1)–Zn(1)–N(2) 76.82(10)°, N(4)–Zn(1)–N(3) 76.71(1)° in (**1**) are similar to those in $[Zn(phen)_2(H_2O)_2]^{2+}$(average 76.8(1)°), but a bit smaller than the reported in $[Zn(H_2O)_4(phen)]^{2+}$ 79.34(1)°. The ligand (Cl₄phen) shows a slightly twisted conformation in $Zn(Cl_4phen)_2(H_2O)_2^{2+}$, in which four chlorine atoms at 3,4,7,8-positions and two hydrogen atoms at 5,6-positions deviate from planarity. The deviation from planarity has also been observed in $Ag(ocp)_2^+$ (ocp = octachloro-1,10-phenanthroline) by Christoph Titze et al. [14]. And the appropriate reasons for the deviation from planarity are the nonbonded interactions between chloride atoms.

Meanwhile, there are a large number of intra- and inter-molecular O–H···O and weak C–H···O hydrogen bonds in the crystal structure of complex (**1**). Two oxygen atoms of nitrate radical anion (O6 and O7) are hydrogen bonded to two hydrogen atoms (H28 and H29) of chelating water molecule from two different units. Every mononuclear unit is linked to other ones via extended Zn–O–H···O–N–O···H–O–Zn bridge to form one-dimensional (1D) infinite chain of hydrogen bond system (Fig. 5). The distances of H···O in O2–H29···O6 and O1–H28···O7 are 2.699 and 2.743 Å, respectively. Then, two 1D infinite chains were

linked by the other free nitrate radical anion to form 2D network. Two oxygen atoms (O5 and O3) of nitrate radical anion form weak C–H···O hydrogen bonds with two hydrogen atoms of Cl₄phen at 5,6-positions, with the bond length (H···O) 3.209 and 3.300 Å, respectively. Meantime, O5 forms hydrogen bond with H27 as well, with the bond

**Table 3** Selected Bond lengths [Å] and angles [°] for complex (**1**)

C(2)–C(l4)	1.711(1)	C(14)–Cl(5)	1.718(1)
C(3)–C(l3)	1.717(1)	C(15)–Cl(6)	1.724(1)
C(8)–Cl(1)	1.719(1)	C(21)–Cl(7)	1.715(1)
C(9)–Cl(2)	1.709(1)	C(20)–Cl(8)	1.713(1)
Zn(1)–O(2)	2.061(2)	Zn(1)–O(1)	2.090(2)
Zn(1)–N(2)	2.139(3)	Zn(1)–N(3)	2.141(2)
Zn(1)–N(1)	2.170(2)	Zn(1)–N(4)	2.170(3)
O(2)–Zn(1)–O(1)	89.41(1)	O(2)–Zn(1)–N(2)	94.46(1)
O(1)–Zn(1)–N(2)	94.10(1)	O(2)–Zn(1)–N(3)	92.36(1)
O(1)–Zn(1)–N(3)	91.90(9)	N(2)–Zn(1)–N(3)	171.12(1)
O(2)–Zn(1)–N(1)	171.02(1)	O(1)–Zn(1)–N(1)	89.59(9)
N(2)–Zn(1)–N(1)	76.92(1)	N(3)–Zn(1)–N(1)	96.80(1)
O(2)–Zn(1)–N(4)	90.70(1)	O(1)–Zn(1)–N(4)	168.61(9)
N(2)–Zn(1)–N(4)	97.25(1)	N(3)–Zn(1)–N(4)	76.81(1)
N(1)–Zn(1)–N(4)	92.03(9)	Zn(1)–O(1)–H(27)	110.3(1)
Zn(1)–O(1)–H(28)	116.5(1)	H(27)–O(1)–H(28)	105.8(1)
Zn(1)–O(2)–H(29)	129.3(1)	Zn(1)–O(2)–H(30)	115.2(1)
H(29)–O(2)–H(30)	106.4(1)		
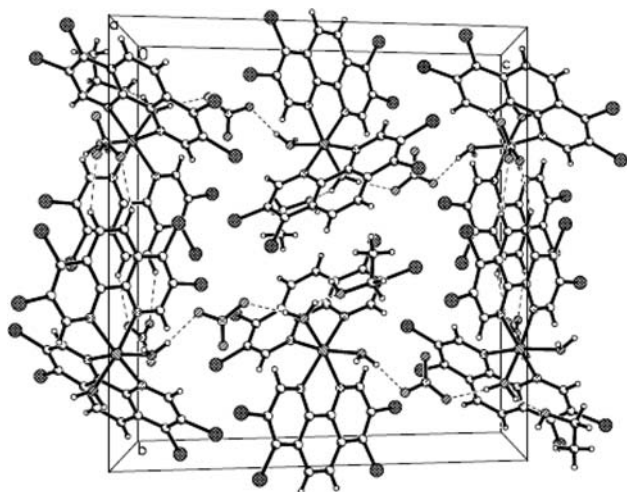
Fig. 5 Diagram of (**1**) illustrating hydrogen bonging interactions between coordination water and NO_3^- along *a*-axis

Table 4 Hydrogen-bonds for 1[Å and (°)] complex (**1**)

D–H	d(D–H)	d(H⋯A)	<DHA	d(D⋯A)	A[symmetry operations]
O1–H27	0.850	1.895	173.22	2.741	O5 [−x, −y+1, −z]
O1–H28	0.850	1.897	173.12	2.743	O7 [x, y, z − 1]
O2–H29	0.850	1.851	174.90	2.699	O6 [x, −y+1/2, z − 1/2]
O2–H30	0.850	2.056	127.51	2.660	O9 [x − 1, y, z − 1]
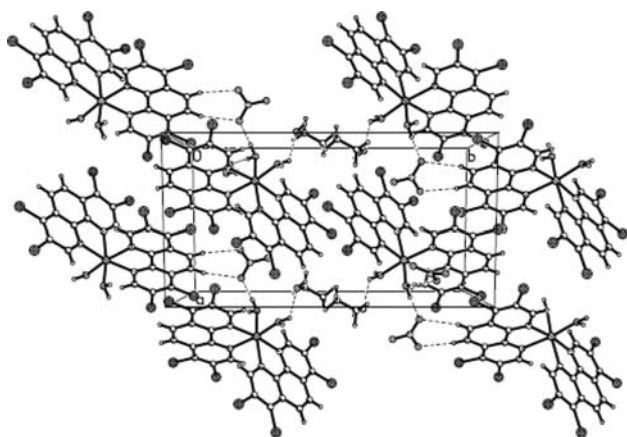
Fig. 6 Diagram of (**1**) illustrating hydrogen bonding interactions between non-bonded ethanol molecular and NO_3^- as well as π interactions along *c*-axis

length 2.741 Å (Table 4). The phenanthroline moieties of the neighboring infinite chains are parallel with each other (Fig. 6). The minimum distance between two phenanthroline moieties is ∼3.455(1) Å. It indicates that the neighboring units are connected via π-stacking interactions. Similar interactions are observed in zinc hydrogen aconitate 1D polymers [24], in which the distance between the

least square planes is 3.496 Å. The strong O–H⋯O hydrogen bonds, weak close C–H⋯O contacts and π-stacking interactions stabilize the structure to form the three-dimensional (3D) network as shown in Fig. 6.

Conclusions

The new Zn(II) complex [Zn(Cl₄phen)₂(H₂O)₂](NO₃)₂·CH₃CH₂OH (**1**) has been obtained and characterized by single crystal X-ray diffraction. The data of crystal structure reveal that multidimensional supramolecular structure has assembled via O–H⋯O and weak C–H⋯O hydrogen bonds, and π-stacking interactions. All these interactions have played a significant role in the crystal structure. The result of spectroscopic absorption and photoluminescence suggest that complex (**1**) has a solvent-dependency effect.

Supplementary Material

CCDC-69984 contains the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 (0)1223-336033; email: deposit@ccdc.cam.ac.uk).

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