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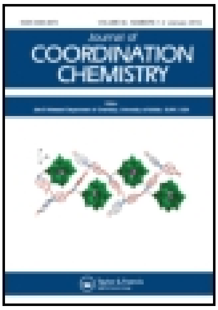

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Syntheses, crystal structures, and properties of four transition metal complexes based on 5-nitro-8-hydroxyquinoline

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Syntheses, crystal structures, and properties of four transition metal complexes based on 5-nitro-8-hydroxyquinoline

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Four new complexes, $[M(C_9H_5N_2O_3)_2(H_2O)_2]\cdot CH_3OH$ (M = Zn(II), Cd(II) and Mn(II)) (**1–3**) and $[Cu(C_9H_5N_2O_3)_2]$ (**4**), have been synthesized by reactions of 5-nitro-quinoline-8-yl acetate (NQA) and corresponding metal salts at room temperature and characterized by elemental analysis, IR, thermal gravimetric analysis (TGA), fluorescence measurement and single crystal X-ray diffraction. **1–3** are mononuclear, further extended to 2-D layers by hydrogen bonds. For **4**, Cu^{2+} is coordinated by two N atoms and two O atoms from two NQ ligands. TGA indicates that **1–4** have good thermal stabilities. Furthermore, **1** and **2** show excellent luminescence in the solid state at room temperature.

Keywords: 8-Hydroxyquinoline; Metal complexes; Luminescence properties

1. Introduction

The design, synthesis, and characterization of organic light emitting diodes (OLEDs) have received considerable attention [1–4]. Tris(8-hydroxyquinolinolate)aluminum(III) (Alq_3), as an electron transporter and photon emitter in OLEDs, was first reported by Tang and VanSlyke [5, 6]. Since then, a large number of reports have been published concentrating on the design and characterization of luminescent metal complexes bearing 8-hydroxyquinoline and its derivatives as ligands. 8-Hydroxyquinoline is one of the best green luminescent materials in OLEDs, chelating many metal ions, and the corresponding complexes possess high luminescence efficiency and quantum efficiency [7]. The emission color and charge-transporting properties of this class of emitting molecules can be changed by varying the central metal ion, the structure, and the coordination number of ligands [8, 9].

In order to retain excellent photoelectron properties of 8-hydroxyquinoline, much progress in modification of 8-hydroxyquinoline complexes has been made, for example, electron-donating/withdrawing groups substituted at 2, 5, or 7 position of 8-hydroxyquinoline, or coordination with different metal ions [10–14]. However, there is a lack of systematic study on complexes based on 5-nitro-8-hydroxyquinoline (NQ). Rik Van Deun's group has

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reported that visible-light-sensitizable near-infrared emission can be obtained from neodymium(III) and ytterbium(III) complexes of NQ in aqueous solution [15]. Jon Zubieta and co-workers have explored a series of '3 + 2' and '2 + 2 + 1' mixed-ligand complexes carrying NQ as the bidentate N, O donor [16]. Thus, detailed structural information of transition metal complexes of this interesting ligand is provided here for the first time. Comparing with NQ, 5-nitro-quinoline-8-yl acetate (NQA) possesses higher solubility in many organic solvents and the hydrolysis of NQA may also provide a better reaction environment for the formation of complexes.

Herein, we report syntheses and crystal structures of four new complexes, [M $(C_9H_5N_2O_3)_2(H_2O)_2]\cdot CH_3OH$ (M = Zn(II), Cd(II) and Mn(II)) (**1–3**) and $[Cu(C_9H_5N_2O_3)_2]$ (**4**), from NQA and corresponding metal salts. **1** and **2** have good thermal stabilities and excellent emission properties which render them for potential applications in electron-transport and luminescent materials.

2. Experimental

2.1. *General*

All reagents were purchased commercially and used without purification. Deionized water was used for the conventional synthesis. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. IR spectra were recorded from 4000 to 400 cm^{-1} with a Bruker TENOR 27 spectrophotometer using KBr pellets. Thermal gravimetric analysis (TGA) was performed on a NETZSCH TG 209 instrument with a heating rate of 10 °C min^{-1}. Fluorescence spectra were measured on an F-4500 fluorescence spectrophotometer with a xenon arc lamp as the light source.

2.2. *Synthesis of NQA and the complexes*

NQA was synthesized in 90% yield by acetylation of NQ by acetic anhydride [17].

2.2.1. Synthesis of $[M(C_9H_5N_2O_3)_2(H_2O)_2]\cdot CH_3OH$ (M = Zn(II), Cd(II) and Mn(II)) (1–3). A methanol solution of NQA (0.0069 g, 0.03 mmol) was added to an aqueous solution of $Zn(NO_3)_2 \cdot 6H_2O$ (0.0045 g, 0.015 mmol). The reaction mixture was stirred for 2 h. Yellow rectangular crystals of **1** were obtained after the solution was allowed to stand at room temperature for 7 days. Yield: 0.0045 g, 55% based on Zn. Elemental analysis, found C, 44.08; H, 4.05; N, 10.32%; calcd. for $C_{20}H_{22}ZnN_4O_{10}$ (fw = 543.82) C, 44.17; H, 4.07; N, 10.30%. IR (KBr, cm^{-1}): 3438vs, 3058w, 1600w, 1567m, 1508m, 1478s, 1386m, 1281vs, 1145s, 741m, 503m, 462m.

Complex **2** was prepared by a similar method to **1** only using $Cd(NO_3)_2 \cdot 4H_2O$ (0.0046 g, 0.015 mmol) instead of $Zn(NO_3)_2 \cdot 6H_2O$. Yellow rectangular crystals of **2** were obtained after the solution was allowed to stand at room temperature for 7 days. Yield: 0.0053 g, 60% based on Cd. Elemental analysis, found C, 40.63; H, 3.72; N, 9.46%; calcd. for $C_{20}H_{22}CdN_4O_{10}$ (fw = 590.82) C, 40.66; H, 3.75; N, 9.48%. IR (KBr, cm^{-1}): 3439vs, 3058w, 1603w, 1509m, 1469s, 1385m, 1284vs, 1142s, 738m, 543m, 440m.

Complex **3** was prepared by a similar method to **1** only using $Mn(OAc)_2 \cdot 4H_2O$ (0.0037 g, 0.015 mmol) instead of $Zn(NO_3)_2 \cdot 6H_2O$. Orange rectangular crystals of **3** were obtained after the solution was allowed to stand at room temperature for 7 days. Yield:

0.0046 g, 58% based on Mn. Elemental analysis, found C, 45.01; H, 4.14; N, 10.55%; calcd. for $C_{20}H_{22}MnN_4O_{10}$ (fw = 533.35) C, 45.04; H, 4.16; N, 10.51%. IR (KBr, cm^{-1}): 3446vs, 3057w, 1600w, 1565m, 1508s, 1471s, 1386m, 1284vs, 1143s, 740m, 569m, 451m.

2.2.2. Synthesis of [Cu($C_9H_5N_2O_3$)$_2$] (4). A methanol solution of $CuSO_4 \cdot 5H_2O$ (5 mg, 0.02 mmol) was carefully layered onto a DMF solution of NQA (4.6 mg, 0.02 mmol). After keeping the solution at room temperature for 1 week, black green rectangular crystals were obtained by slow evaporation. Yield: 0.0034 g, 38% based on Cu. Elemental analysis, found C, 48.91; H, 2.27; N, 12.69%; calcd. for $C_{18}H_{10}CuN_4O_6$ (fw = 441.84) C, 48.93; H, 2.28; N, 12.68%. IR (KBr, cm^{-1}): 3100w, 1600w, 1566m, 1502s, 1462s, 1391m, 1264vs, 1149s, 745m, 580m, 482m.

2.3. *X-ray crystallography*

Diffraction data for **1–4** were collected on a computer-controlled Rigaku Saturn diffractometer. The detector was equipped with graphite-monochromated Mo-K_α radiation (0.71073 Å) by using the ω-scan technique. The structure was solved by direct methods and refined with full-matrix least-squares on F^2 using SHELXS-97 [18] and SHELXL-97 [19]. All nonhydrogen atoms were refined anisotropically. Organic hydrogens and water hydrogens were assigned with common isotropic displacement factors and included in the final refinement by geometrical restraints. The crystallographic data, selected bond lengths, and angles for **1–4** are given in tables 1 and 2, respectively, hydrogen bond parameters are provided in table 3.

3. Results and discussion

3.1. *Crystal structures of 1–4*

3.1.1. [M($C_9H_5N_2O_3$)$_2$ (H_2O)$_2$]·CH_3OH (M = Zn(II), Cd(II) and Mn(II)) (1–3). X-ray diffraction structure analyses reveal that **1** and **2** are isomorphous. Compared with **1** and **2**, **3** has the same coordination environment, but shows a different periodic arrangement in the cell (figure 1). Compounds **1–3** are mononuclear complexes which are further extended to 2-D layers by hydrogen bonds. Herein, we discuss the structure of **1** in detail as a representation.

The crystal structure of **1** (figure 2) consists of a centrosymmetric mononuclear [Zn ($C_9H_5N_2O_3$)$_2$(H_2O)$_2$] unit. Zn^{2+} is distorted octahedral with the equatorial plane occupied by N1, N1A, O1 and O1A from two bidentate NQ, and the axial positions are completed by O1W, O1WA from the waters. The coordination bond length in the axial direction [Zn (1)–O(1 W) = 2.1389(18) Å] is longer than that in the equatorial plane [Zn(1)–O(1) = 2.0550(14) Å]. The Zn–N bond length is 2.1317(18) Å, which is close to the values previously reported for similar octahedral complexes [20,21]. [Zn($C_9H_5N_2O_3$)$_2$(H_2O)$_2$] and methanols further construct a [Zn($C_9H_5N_2O_3$)$_2$(H_2O)$_2$] · CH_3OH unit with uncoordinated methanol playing an important role in the formation of hydrogen bonds. Methanol donates H to O3 of the nitro, water donates H to O4 of methanol and O1 of quinoline rings (O(4) ··· O(3) = 2.842(2) Å, ∠O(4)–H(4) ··· O(3) = 172(3)°, O(1W) ··· O(4) = 2.724(2) Å, ∠O (1 W)–H(1W) ··· O(4) = 173(3)°, O(1W) ··· O(1) = 2.688(2) Å, ∠O(1W)–H(2W) ··· O(1) = 175(3)°), forming three kinds of hydrogen bonds. These interactions bridge adjacent [Zn

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Table 1. Crystal data and structure refinement details for **1–4**.

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{20}H_{22}ZnN_4O_{10}$	$C_{20}H_{22}CdN_4O_{10}$	$C_{20}H_{22}MnN_4O_{10}$	$C_{18}H_{10}CuN_4O_6$
Formula weight	543.81	590.83	533.36	441.84
Temperature (K)	113 (2)	293(2)	113 (2)	113 (2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$p-1$	$p-1$	$p-1$	$p2_1/c$
a (Å)	5.1490(10)	5.1724 (10)	5.130 (2)	7.347 (3)
b (Å)	8.5460(18)	8.8510 (17)	8.593 (3)	14.788 (6)
c (Å)	12.512 (3)	12.798 (3)	12.703 (5)	7.209 (3)
α (°)	102.93 (3)	103.15 (3)	76.77 (2)	
β (°)	98.10 (3)	97.23 (3)	82.36 (2)	94.676 (7)
γ (°)	90.01 (3)	90.20 (3)	89.36 (2)	
Volume (Å^3)	531.0 (2)	565.7 (2)	540.2 (4)	780.7 (6)
Z	1	1	1	2
Calculated density (Mg m^{-3})	1.701	1.734	1.640	1.880
Absorption coefficient (mm^{-1})	1.225	1.030	0.679	1.452
$F(000)$	280	298	275	446
Crystal size (mm)	0.20 × 0.10 × 0.10	0.20 × 0.18 × 0.12	0.20 × 0.18 × 0.12	0.16 × 0.12 × 0.08
θ Range for data collection (°)	1.69–25.00	1.69–25.00	1.66–27.00	2.75–27.86
Limiting indices	$-6\leq h\leq 6$ $-11\leq k\leq 11$ $-16\leq l\leq 15$	$-6\leq h\leq 6$ $-10\leq k\leq 9$ $0\leq l\leq 14$	$-6\leq h\leq 6$ $-11\leq k\leq 11$ $-16\leq l\leq 16$	$-9\leq h\leq 9$ $-19\leq k\leq 19$ $-9\leq l\leq 9$
Reflections collected	5631	1853	5699	8003
Independent reflection	1930 [R(int) = 0.0370]	1853 [R(int) = 0.0000]	2365 [R(int) = 0.0362]	1864 [R(int) = 0.0397]
Max. and min. transmission	0.885 and 0.863	0.8798 and 0.8107	0.9230 and 0.8762	0.8927 and 0.8009
Data/restraints/parameters	1843/0/193	1994/0/193	2345/0/193	1864/0/133
Goodness-of-fit on F^2	1.033	1.036	1.113	1.064
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0244$ $wR_2 = 0.0570$	$R_1 = 0.0050$ $wR_2 = 0.0137$	$R_1 = 0.0265$ $wR_2 = 0.0562$	$R_1 = 0.0384$ $wR_2 = 0.0791$
R indices (all data)	$R_1 = 0.0286$ $wR_2 = 0.0580$	$R_1 = 0.0050$ $wR_2 = 0.0137$	$R_1 = 0.0355$ $wR_2 = 0.0576$	$R_1 = 0.0453$ $wR_2 = 0.0825$
Largest diff. peak and hole (e Å^{-3})	0.306 and −0.390	0.220 and −0.076	0.260 and −0.324	0.521 and −0.559

$(C_9H_5N_2O_3)_2(H_2O)_2] \cdot CH_3OH$ units to give 2-D layers, depicted in figure 3. Furthermore, two pyridine rings arrange in a parallel fashion to result in π–π stacking interactions with face-to-face distance of 3.3792 Å; a similar π–π stacking exists in two quinoline rings with face-to-face distance of 3.3471 Å (figure 4).

3.1.2. $[Cu(C_9H_5N_2O_3)_2]$ (4).

Complex **4** is a mononuclear structure, as shown in figure 5. Single-crystal X-ray diffraction analysis reveals that Cu^{2+} is coordinated by N1, N1A, O1 and O1A from two NQ ligands. Bond lengths of Cu1–N1 and Cu1–O1 are 1.9575(17) and 1.9411(15) Å, respectively. The angles of N(1)A–Cu(1)–N(1) and O(1)–Cu(1)–O(1)A are 180.0° and the angles of O(1)–Cu(1)–N(1)A and O(1)–Cu(1)–N(1) are 95.95(7)° and 84.05(7)°, respectively, revealing that Cu(II) is in a rectangle geometry [22]. Quinoline rings are stacked in relation to each other with the centroid-to-centroid distance of 3.609 Å, resulting in a 2-D structure in the *bc* plane (figure 6).

Table 2. Selected bond lengths (Å) and angles (°) for **1**–**4**.

Compound **1**			
Zn(1)–O(1)	2.0550(14)	O(1)#1–Zn(1)–O(1W)	90.35(6)
Zn(1)–N(1)	2.1317(18)	N(1)–Zn(1)–O(1W)	91.98(7)
Zn(1)–O(1W)	2.1389(18)	N(1)#1–Zn(1)–O(1W)	88.02(7)
O(1)–Zn(1)–N(1)	79.29(6)	C(8)–N(1)–Zn(1)	129.21(14)
O(1)–Zn(1)–O(1W)	89.66(6)	C(1)–O(1)–Zn(1)	114.18(12)
O(1)–Zn(1)–N(1)#1	100.71(6)	C(9)–N(1)–Zn(1)	111.96(13)
O(1)–C(1)–C(2)	122.99(19)	O(1)–C(1)–C(9)	120.09(18)
Compound **2**			
Cd(1)–O(1)	2.2373(7)	O(1)#1–Cd(1)–N(1)	106.95(3)
Cd(1)–N(1)	2.3183(10)	N(1)#1–Cd(1)–O(1W)#1	91.43(3)
Cd(1)–O(1W)	2.3439(8)	O(1)–C(1)–C(2)	122.22(5)
O(1)–Cd(1)–N(1)	73.05(3)	O(1)–C(1)–C(9)	121.13(5)
O(1)–Cd(1)–O(1W)	88.74(3)	C(9)–N(1)–Cd(1)	113.72(4)
O(1)#1–Cd(1)–O(1W)	91.26(3)	C(8)–N(1)–Cd(1)	126.88(4)
N(1)#1–Cd(1)–O(1W)	88.57(3)	C(1)–O(1)–Cd(1)	116.27(4)
Compound **3**			
Mn(1)–O(1)	2.1275(12)	O(1)#1–Mn(1)–N(1)	104.57(5)
Mn(1)–N(1)	2.2612(15)	N(1)#1–Mn(1)–O(1W)#1	89.27(5)
Mn(1)–O(1W)	2.2023(13)	O(1)–C(1)–C(2)	122.86(15)
O(1)–Mn(1)–N(1)	75.43(5)	O(1)–C(1)–C(9)	119.91(15)
O(1)–Mn(1)–O(1W)	90.92(5)	C(9)–N(1)–Mn(1)	112.33(10)
O(1)#1–Mn(1)–O(1W)	89.08(5)	C(8)–N(1)–Mn(1)	128.73(11)
N(1)#1–Mn(1)–O(1W)	90.73(5)	C(1)–O(1)–Mn(1)	117.12(10)
Compound **4**			
Cu(1)–O(1)	1.9411(15)	C(9)–N(1)–Cu(1)	111.48(13)
Cu(1)–N(1)	1.9575(17)	C(8)–O(1)–Cu(1)	112.42(13)
O(1)#1–Cu(1)–N(1)#1	84.05(7)	C(1)–N(1)–Cu(1)	128.30(16)
O(1)–Cu(1)–N(1)#1	95.95(7)	O(1)–Cu(1)–N(1)	84.05(7)

Table 3. Selected H-bond lengths (Å) and angles (°) for **1**–**3**.

D–H ··· A	*d*(D–H)	*d*(H ··· A)	*d*(D ··· A)	∠(DHA)
Compound **1**				
O(1W)–H(2W) ··· O(1)$^{\mathrm{i}}$	0.72(2)	1.97(2)	2.688(2)	175(3)
O(1W)–H(1W) ··· O(4)	0.80(2)	1.93(2)	2.724(2)	173(3)
O(4)–H(4) ··· O(3)$^{\mathrm{ii}}$	0.73(2)	2.12(2)	2.842(2)	172(3)
Compound **2**				
O(1W)–H(2W) ··· O(1)$^{\mathrm{i}}$	0.852(11)	1.826(11)	2.6774(10)	176.6(10)
O(1W)–H(1W) ··· O(4)	0.852(11)	1.890(11)	2.7387(9)	174.3(11)
O(4)–H(4) ··· O(3)$^{\mathrm{ii}}$	0.811(10)	2.056(10)	2.8648(12)	174.4(10)
Compound **3**				
O(1W)–H(1W) ··· O(4)$^{\mathrm{i}}$	0.803(19)	1.920(19)	2.7223(17)	177(2)
O(1W)–H(2W) ··· O(1)$^{\mathrm{ii}}$	0.803(19)	1.879(19)	2.6813(17)	176.9(19)
O(4)–H(4) ··· O(2)$^{\mathrm{iii}}$	0.835(17)	2.025(17)	2.8517(18)	170.6(18)

Symmetry transformations used to generate equivalent atoms: for **1**: (i) $x+1$, y, z, (ii) $-x+1$, $-y+1$, $-z+1$, for **2**: (i) $x+1$, y, z, (ii) $-x+1$, $-y+1$, $-z+1$, for **3**: (i) $-x+1$, $-y+1$, $-z+1$, (ii) $-x$, $-y+1$, $-z+1$, (iii) $-x+1$, $-y+1$, $-z$.

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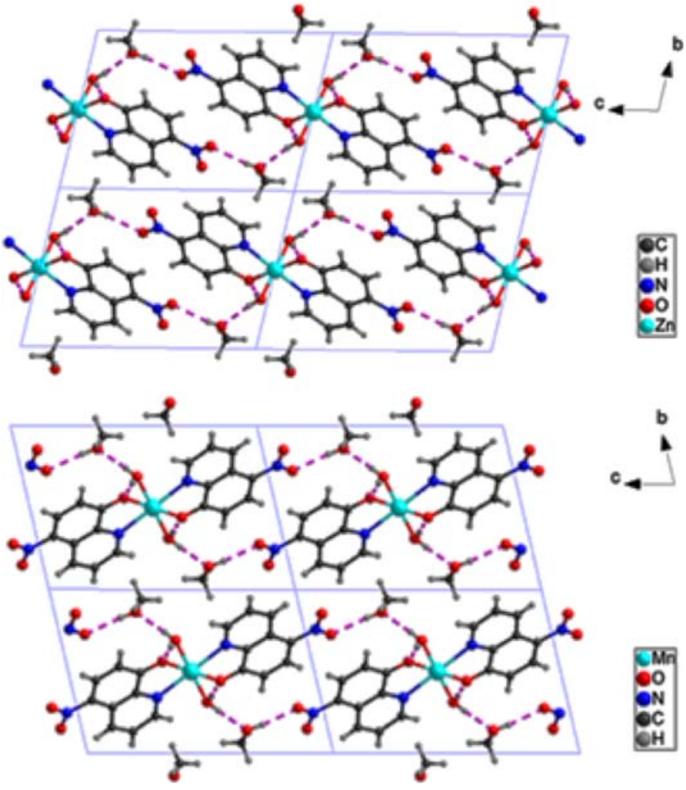

Figure 1. The different molecule arrangements in unit cells of **1** and **3**.

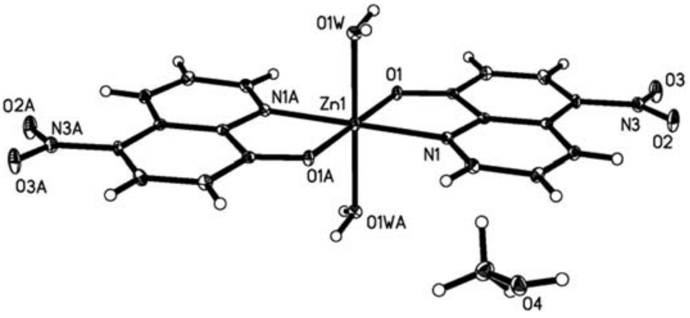

Figure 2. ORTEP of **1** showing the molecular structure with 30% probability thermal ellipsoids. Symmetry code for A: $1-x$, $1-y$, $-z$.

3.2. *IR spectra*

The IR spectra of **1–4** (4000–400 $\mathrm{cm^{-1}}$) were investigated. In the region below 1700 $\mathrm{cm^{-1}}$, positions and intensities of the bands generated by the quinoline ligands are very similar. The absence of the characteristic band around 1200 $\mathrm{cm^{-1}}$ is attributed to the $\nu_{\mathrm{C\text{–}O}}$ of the complexes. Weaker bands at 500 and 450 $\mathrm{cm^{-1}}$ are assigned to $\nu_{\mathrm{M\text{–}N}}$ and $\nu_{\mathrm{M\text{–}O}}$ after the ligand is coordinated with metal, respectively. For **1–3**, the strong and broad absorption

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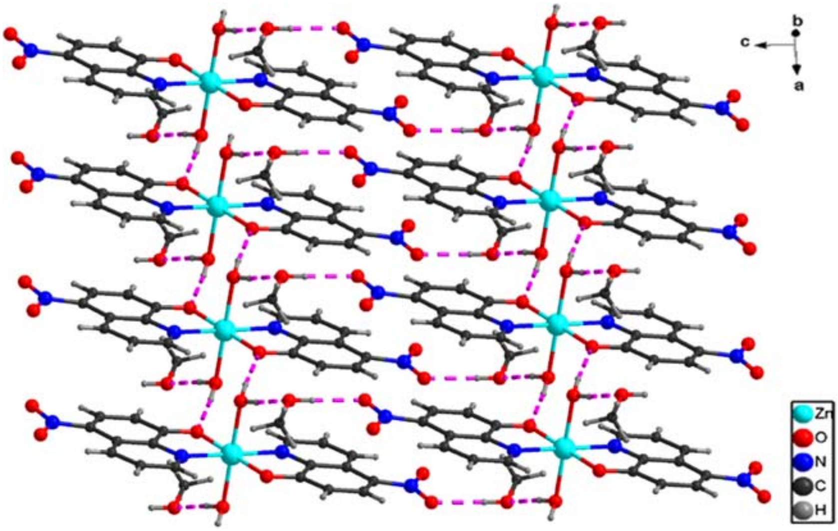

Figure 3. The 2-D layers of **1** via hydrogen bond interactions.

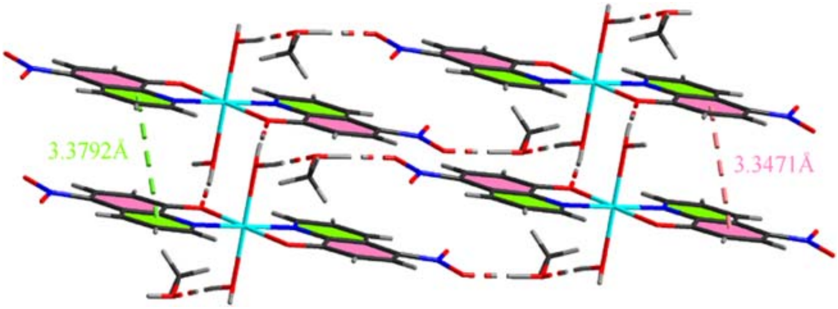

Figure 4. The interlayer face-to-face π–π stacking interactions of **1**.

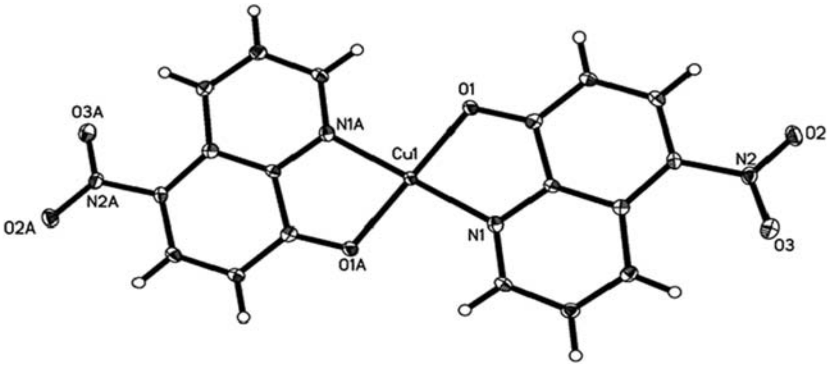

Figure 5. ORTEP of **4** showing the molecular structure with 30% probability thermal ellipsoids. Symmetry code for A: 1−*x*, −*y*, −z.

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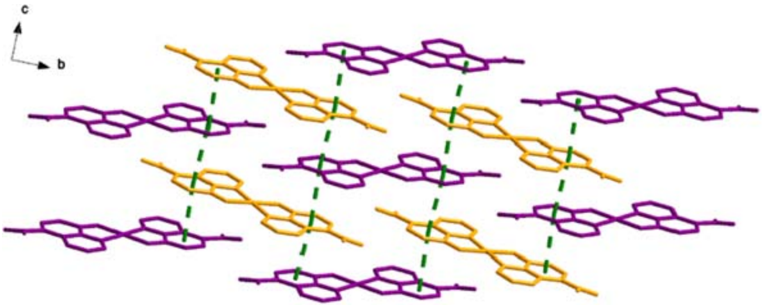

Figure 6. The π–π interactions (dashed lines) in **4** (centroid-to-centroid distance of 3.609 Å).

band at 3440 cm^{-1} is attributed to $\nu_{O–H}$ of coordinated water. IR spectra of the complexes are consistent with the crystal structures.

3.3. *Thermal gravimetric analysis (TGA)*

TGA was carried out for **1–4** from 20 to 800 °C under air (Supplementary Material). For **1–3**, the first weight losses at 60–147 °C are 17.38, 15.22, and 17.61%, respectively, due to loss of two coordinated waters and one uncoordinated methanol (calcd. 12.87, 11.84, 13.12% for **1–3**, respectively). From 147 to 396 °C, there are no weight changes in the TGA curves. The second weight loss above 396 °C corresponds to decomposition of the complexes. For **4**, there is no significant weight loss from 20 to 370 °C. Above 370 °C, an obvious weight loss (71.94%) occurs, corresponding to decomposition of **4**. After 504 °C, no weight loss is observed. The residual should be CuO.

3.4. *The fluorescent properties*

Complexes of d^{10} transition metal possess varied luminescent properties. Ligands and their coordination modes obviously affect emission and luminescent mechanisms. To study the

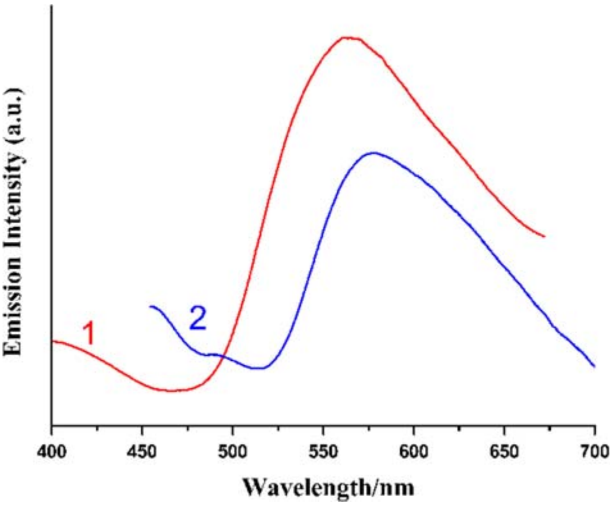

Figure 7. Emission spectra for **1** and **2** in the solid state at room temperature.

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luminescence of **1** and **2**, fluorescence was performed at room temperature in the solid state. Spectra of **1** and **2** display yellow/green emissions at 565 nm ($\lambda_{ex} = 360$ nm) and 574 nm ($\lambda_{ex} = 398$ nm), respectively (figure 7). Compared with NQA, the strong emission bands of **1** and **2** are red-shifted 82 and 91 nm, possibly attributed to lowering of the energy gap between π and π^* with the formation of N–Zn/Cd and O–Zn/Cd bonds. The electrons in the full d-orbitals of Zn^{2+}/Cd^{2+} are accessible for back bonding to π-acceptor ligands, which can result in emissions assigned to the metal-to-ligand charge transfer transition [23, 24].

ZnQ_2 (Q = 8-hydroxyquinoline) is an excellent electron-transporting material and widely used as luminescent materials [25–28]. The emission band of **1** is 23 nm red-shifted in comparison with the emission band of ZnQ_2 ($\lambda_{ex} = 380$ nm) [29]. Due to the similarity of the structure and luminescent emission spectra, we expect complexes based on NQA can be useful in electron-transport and luminescent materials.

4. Conclusion

Starting from NQA, four transition metal complexes based on NQ have been synthesized, characterized and their fluorescent properties studied. Comparing with NQ, NQA possesses higher solubility in many organic solvents and the hydrolysis of NQA may also provide a better reaction environment for the formation of complexes. Complexes **1–4** show excellent thermal stabilities. Complexes **1** and **2** show yellow/green fluorescent emissions at room temperature and may be candidates for electron-transport and luminescent materials.

Supplementary material

CCDC-875250 for **1**, CCDC-875251 for **2**, CCDC-875249 for **3** and CCDC-875248 for **4**, and contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB21EZ, UK; Fax: (+44) 1223 336 033; or E-mail: deposit@ccdc.cam.ac.uk).Supplementary material

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