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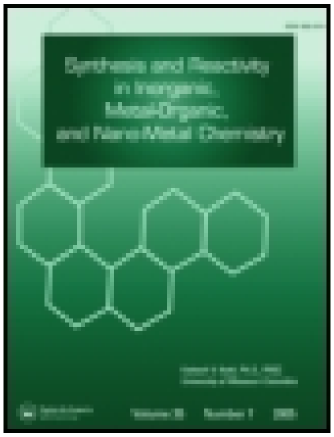

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Synthesis, Crystal Structures and Characterizations of Two Zn(II) Coordination Polymers Base on a Reduced Schiff-base Ligand

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ABSTRACT

Two coordination polymers base on a reduced Schiff-base ligand, namely, $[Zn_2((OOC)_2C_6H_3NHCH_2C_6H_4COOH)_2(C_{10}H_8N_2)(H_2O)_2]\cdot 3H_2O$ (**1**) and $[Zn_2((OOC)_2C_6H_3NHCH_2C_6H_4COO)(C_{10}H_8N_2)_2(HCOO)(H_2O)]\cdot H_2O$ (**2**) have been obtained by hydrothermal method and structurally characterized. These two compounds crystallize in the $P2_1/c$ space group. Compound **1** exhibits a double-chain structure while compound **2** exhibit a layer structure. Photoluminescent investigation shows that compounds **1** and **2** displays strong emission in the yellow region.

Keywords: Reduced Schiff-bases; Photoluminescence; Crystal structure.

INTRODUCTION

In recent years, metal coordination polymers(CPs) which are formed by metal ions and organic ligands have been put much attention because of their potential applications in catalysis, ion exchange, proton conductivity, intercalation chemistry, photochemistry, gas sorption, selective separation, magnetic, electronic, nonlinear optical and materials chemistry [1-9]. Lots of CPs which exhibit a variety of infinite or discrete frameworks of 1D, 2D or 3D structures have been reported [10-12]. We can divide the organic ligands into two categories: rigid (such as Terephthalic acid [13]) and flexible (semi-rigid or non-rigid, such as succinic acid [14]) ligands according to the properties of the organic ligands. Compared to the rigid ligands, using flexible ligands to construct CPs is more difficult because of the less predictable assembly process. However, due to the sensitivity and diversification of the flexible ligands, they can afford good opportunities to investigate the details of the self-assembly process and provide more information on the directional synthesis of the target CPs [15-16]. The reduced Schiff-bases is a sort of good flexible ligands. Their flexible skeleton can freely twist around the –NH-CH_2–groups. Up to now, to the best of our knowledge, the coordination polymers base on the reduced Schiff-bases which formed by the aminobenzoic acid and the carboxybenzaldehyde is still few. Ligands of this type have two or three carboxylate groups at the terminal positions and a secondary amine group between the phenyl groups, so they can show various coordination modes. Professor Jian-Fang Ma's group has reported a series compounds base on the reduced Schiff-base of this type and the flexible 1,4-bis(1H-imidazol-1-yl)butane ligand [17]. In order to study the coordination chemistry of reduced Schiff-base ligands of this type, in this paper, we have synthesized a reduced Schiff-base ligand which formed by 5-aminoisophthalic acid and 4-carboxybenzaldehyde. Two Zinc(II) compounds have been obtained base on this ligand with the present of 4,4'- bipyridine or 2,2'-bipyridine. Herein we report their syntheses, characterizations, and crystal structures.

EXPERIMENTAL

Materials and instruments

All the chemicals were obtained from commercial sources and used without further purification. Elemental analyses of C, H, N were performed on a German Elementary Vario EL III instrument. The FT-IR spectra were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer using KBr pellets in the range of 4000-400 cm^{-1}. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 10^{o}C /min under a nitrogen atmosphere in the range of room temperature to 900°C. Photoluminescence spectra were collected on an Edinburgh FLS920 spectrometer equipped with a continuous Xe900 Xenon lamp at room temperature.

Synthesis of $(HOOC)_2C_6H_3NHCH_2C_6H_4(COOH)$, H_3L

H_3L was synthesized according to the procedures previously described [18-20]. A mixture of KOH (50 mmol, 2.80 g) and 5-Aminoisophthalic acid (25 mmol, 4.48 g) in 30 mL CH_3OH/H_2O (V:V = 5:1) was stirred for 30 minutes at room temperature. A mixture of KOH (25 mmol, 1.40 g) and 4-carboxybenzaldehyde (25 mmol, 3.75 g) in 40 mL CH_3OH was stirred for 30 minutes at room temperature, too. Then the latter was added slowly into the former by stirring. The resulting solution was refluxed for 6 h. Then excess $NaBH_4$ was added after the solution was cooled in an ice bath. After 30 minutes, the solution was acidified with concentrated HCl to a pH of 3.5-5.0. The resulting solid was filtered off, washed with water and ethanol, and recrystallized from water/ethanol (1:1) (yield 75%). ESI-MS (methanol) m/z: 313.9, $[M-H]^-$.

Synthesis of $[Zn_2(HL)_2(4,4'\text{-bipy})(H_2O)_2]\cdot 3H_2O$ (1)

A mixture of $Zn(NO_3)_2\bullet 6H_2O$ (0.089 g, 0.3 mmol), H_3L (0.063 g, 0.2 mmol), 4,4'-bipyridine (0.031 g, 0.2 mmol), 1 mL N, N-dimethylformamide (DMF) and 9 mL deionized water was sealed into a steel bomb equipped with a Teflon liner (15 mL), and then heated at 120 ºC for 4 days. Light brown needle crystals of compound **1** were recovered in ca. 45% yield based on Zn. Elemental analyses for **1**, $C_{42}H_{40}N_4O_{17}Zn_2$ (Mr = 1003.52): C, 50.08; H, 4.17; N, 5.53%; Calcd.: C, 50.22; H, 3.99; N, 5.58%. IR data (KBr, cm^{-1}): 3441(s), 1610(s), 1550(s), 1460(s), 1418(s), 1364(s), 1221(m), 1148(m), 1072(m), 1016(m), 818(m), 787(m), 762(m), 729(m), 692(m), 642(m), 629(m).

Synthesis of $[Zn_2(L)(2,2'\text{-bipy})_2(HCOO)(H_2O)]\cdot H_2O$ (2)

A mixture of $Zn(NO_3)_2\bullet 6H_2O$ (0.060 g, 0.2 mmol), H_3L (0.032 g, 0.1 mmol), 2,2'-bipyridine (0.031 g, 0.2 mmol), 1 mL DMF and 9 mL deionized water was sealed into a steel bomb equipped with a Teflon liner (15 mL), and then heated at 120 ºC for 3 days. A few light brown block crystals of compound **2** were recovered in ca. 30% yield based on Zn. Elemental analyses for **2**, $C_{37}H_{31}N_5O_{10}Zn_2$ (Mr = 836.41): C, 53.22; H, 3.87; N, 8.43%; Calcd.: C, 53.08; H, 3.71; N, 8.37%. IR data (KBr, cm^{-1}): 3443(m), 3314(m), 1703(s), 1589(s), 1418(s), 1364(m), 1315(m), 1252(m), 1175(m), 1105(m), 1030 (w), 868(m), 766(s), 733(m), 704(m).

Structure determination

Single crystal of compounds **1** (size: 0.40*0.06*0.04 mm) and **2** (size: 0.25*0.22*0.18 mm) were mounted on a Bruker Smart Apex CCD diffractometer equipped with a graphite-monochromated Mo-Ka radiation (λ = 0.71073 Å) respectively. Intensity data for the two compounds were collected using ω-scans at 293 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption by SADABS program. The structure was solved by direct methods using SHELXS-97[21] and refined on F^2 by full-matrix least-squares procedure with SHELXL-97 program[22]. The difference Fourier maps based on these atomic positions yield the non-hydrogen atoms. The hydrogen atoms were located at the geometrically calculated positions. Crystallographic data and structural refinements are summarized in Table 1. Selected bond lengths are listed in Table 2 for compounds **1** and **2**. More details about the crystallographic data have been deposited as supplementary materials.

RESULTS AND DISCUSSION

Crystal structure

As shown in Fig. 1, compound **1** contains one Zn(II) ion, a HL anion and one-half 4,4'-bipy, a coordinated water molecule and one and one and a half lattice water molecules in its an asymmetric unit. The Zn(II) ions are four-coordinated by two oxygen atoms from two HL anions, one oxygen atoms from the coordinated water molecule and one nitrogen atoms from a

4,4'-bipy ligand. The Zn-O distances ranges from 1.904(7) to 2.006(7) Å, the Zn-N distances is 2.006(8)Å, which are comparable to those reported for other Zn(II) compounds [23, 24]. The reduced Schiff-base ligand is bidentate. Two COO^- group of the reduced Schiff-base ligand bridged with a Zn(II) ion respectively. By the bridge of the reduced Schiff-base ligands and the 4,4'-bipyridine, a double-chain structure has formed (Fig. 2). These double-chains are further link into layer structure by the hydrogen bond [O(1)w…O(6), symmetry code: 1-x, y-0.5, 0.5-z, bond distance is 2.675(9) Å] and the π•••π interactions between the pyridyl rings of adjacent 4,4'-bipy [the cg•••cg (center of gravity of the pyridyl ring) distance is 3.66 Å]. Then these layers are stacking into a "V-shape" supramolecular structure (Fig. 3) by the hydrogen bond [O(1)w…O(2), symmetry code: x, y-1, z, bond distance is 2.713(10) Å].

Compound **2** contains two Zn(II) ions, two L anions, a 2,2'-bipy, a formyl (come from the decompose of DMF), a coordinated water molecule and a lattice water molecules in its an asymmetric unit (Fig. 4). Zn(1) is six-coordinated by two nitrogen atoms from a 2,2'-bipy ligand, an oxygen atom from the $HCOO^-$ anions(come from the decomposition of the DMF), three oxygen atoms from two L anions. Zn(2) is six-coordinated((including a weak Zn-O coordinated bond of length 2.469(2) Å) by two nitrogen atoms from a 2,2'-bipy ligand, two oxygen atoms from a $HCOO^-$ anion, an oxygen atom from a L anion and an oxygen atom from the coordinated water molecule. The reduced Schiff-base ligand is tetradentate. Two COO^- group of the reduced Schiff-base ligand bridged with a Zn(II) ion respectively, and one COO^- group chelate with a Zn(II) ion. By the bridge of the reduced Schiff-base ligands, a layer structure has formed (Fig. 5). These layers are further linked into supramolecular structure (Fig. 6) by the hydrogen bonds [O(2)w…O(3), symmetry code: -x, y-0.5, 0.5-z, bond distance is 2.746(3) Å; O(2)w…O(7), symmetry code: x, 1.5-y, 0.5+z, bond distance is 2.833(3) Å] and the π•••π interactions between the pyridyl rings of adjacent 2,2'-bipy [the cg•••cg (center of gravity of the pyridyl ring) distance is 3.72 or 3.74 Å respectively].

TGA studies

The thermal behavior of compounds **1** and **2** were studied to reveal their thermal stability. The thermal curves are exhibited in Fig.7. The TGA curves of compound **1** exhibits three stages weight loss dues to the release of lattice water molecules (from room temperature to 130 ºC, expt.: 5.2%, calcd.: 5.4%), the coordinated water molecules (from 170 ºC to 240 ºC, expt.: 3.6%, calcd.: 3.5%) and the decomposes of the organic ligands (from 290 ºC up to 900 ºC). For **2**, it can stable up to 320 ºC. Then it exhibits a stage of weight loss dues to release or decomposes of the water molecules and the organic ligands. The weight loss of 69.9% is similar to that calculated(70.1%), if the residua is $ZnCO_3$.

Photoluminescent properties

The solid state luminescent emission spectrum of compounds **1, 2** and H_3L at room temperature are depicted in Fig. 8. The H_3L displays emission peaks at 415 nm upon excitation at 315 nm. The compound **1** exhibit emission peaks at 556 nm upon excitation at 372 nm. The compound **2** exhibit emission peaks at 517 nm upon excitation at 370 nm. Compared with the emission spectrum of the H_3L, red shift emissions of compound **1** and **2** have been observed. The emission bands of compounds **1** and **2** are probably originated from the intraligand luminescent emission

[25]. These results indicate that compounds **1** and **2** would be candidates for potential photoactive materials.

CONCLUSION

In summary, by hydrothermal method, we have successfully synthesized two new Zn(II) compounds base on the reduced Schiff-bases ligand, The structural diversities of the these two compounds maybe due to the difference of the present of the second ligand---4,4'-bipy or 2,2'-bipy. The former is a bridged ligand while the latter is a chelated ligand. We hope that other new coordination polymers with intriguing structures as well as physical properties may also be synthesized base on the reduced Schiff-base multidentate carboxylates.

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Supplementary material

CCDC 870367 to 870368 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.)C44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk].

REFERENCES

1. Yaghi, O.M.; O'Keeffe, M.; Ockwig, N.W.; Chae, H.K.; Eddaoudi, M.; Kim J. Reticular Synthesis and The Design of New Materials. *Nature* **2003**, 423, 705-714.
2. Kitagawa, S.; Kitaura, R.; Noro, S. I. Functional Porous Coordination Polymers. *Angew. Chem. Int. Ed.* **2004**, 43, 2334-2375.
3. Zhao, D.; Timmons, D. J.; Yuan, D. Q.; Zhou, H. C. Tuning the Topology and Functionality of Metal-Organic Frameworks by Ligand Design. *Acc. Chem. Res.* **2011**, 44, 123-133.
4. Jiang, H. L.; Xu, Q. Porous Metal–organic Frameworks as Platforms for Functional Applications. *Chem. Commun.* **2011**, 47, 3351-3370.
5. Zhang, Y. B.; Zhang, W. X.; Feng, F. Y.; Zhang, J. P.; Chen, X. M. A Highly Connected Porous Coordination Polymer with Unusual Channel Structure and Sorption Properties. *Angew. Chem. Int. Ed.* **2009**, 48, 5287-5290.
6. Pramanik, S.; Zheng, C.; Zhang, X.; Emge, T. J.; Li, J. New Microporous Metal-Organic Framework Demonstrating Unique Selectivity for Detection of High Explosives and Aromatic Compounds. *J. Am. Chem. Soc.* **2011**, 133, 4153-4155.
7. Wang, C.; Lin, W. Diffusion-Controlled Luminescence Quenching in Metal-Organic Frameworks. *J. Am. Chem. Soc.* **2011**, 133, 4232-4235.
8. Xu, W. T.; Chen, L.; Jiang, F. L.; Hong, M. C. Synthesis, Crystal Structure and Properties of a Nanotubular Metal-organic Framework (MOFs) Based on Cu(II) Oxide Chains and Benzenedicarboxylates. *Chinese J. Struct. Chem.* **2012**, 31, 321-326.

9. Herm, Z. R.; Swisher, J. A.; Smit, B.; Krishna, R.; Long, J.R. Metal-Organic Frameworks as Adsorbents for Hydrogen Purification and Precombustion Carbon Dioxide Capture. *J. Am. Chem. Soc.* **2011**, 133, 5664-5667.

10. Zhang, J. P.; Qi, X. L.; He, C. T.; Wang, Y.; Chen, X. M. Interweaving Isomerism and Isomerization of Molecular Chains. *Chem. Commun.* **2011**, 47, 4156-4158.

11. DeBurgomaster, P.; Ouellette, W.; Liu, H.; O'Connor, C. J.; Zubieta, J. Hydrothermal chemistry of vanadium oxides with aromatic di- and tri-phosphonates in the presence of secondary metal copper(II) cationic complex subunits. *CrystEngComm*, **2010**, 12, 446-469.

12. Ying, S. M.; Mao, J. G. Introducing a Second Ligand: New Route to Luminescent Lanthanide Polyphosphonates. *Cryst. Growth Des.* **2006**, 6, 964-968.

13. Eddaoudi, M.; Kim, J.; Rosi, N.; Vodak, D.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. Systematic Design of Pore Size and Functionality in Isoreticular MOFs and Their Application in Methane Storage. *Science* **2002**, 295, 469-472.

14. Ying, S. M.; Mao, J. G.; Sun, Y. Q.; Zeng, H. Y.; Dong, Z. C. Syntheses and Crystal Structures of Three Open-frameworks of Metal Succinates Containing a 4,4'-Bipyridine Ligand. *Polyhedron* **2003**, 22, 3097-3103.

15. Liu. T.F.; Lü, J.; Cao, R., Coordination Polymers Based on Flexible Ditopic Carboxylate or Nitrogen-donor Ligands. *CrystEngComm* **2010**, 12, 660-670.

16. Chen, C. L.; Zhang, J. Y.; Su, C. Y. Coordination Assemblies of Metallacyclic, Prismatic and Tubular Molecular Architectures Based on the Non-rigid Ligands. *Eur. J. Inorg. Chem.* **2007**, 2997-3010.

17. Liu, Y. Y.; Wang, Z. H.; Yang, J.; Liu, B.; Liu, Y. Y.; Ma, J. F. A Series of Coordination Polymers Based on Reduced Schiff Base Multidentateanions and Bis(imidazole) Ligands: Syntheses, Structures and Photoluminescence. *CrystEngComm* **2011**, 13, 3811-3821.

18. Das, M. C.; Bharadwaj, P. K. A Porous Coordination Polymer Exhibiting Reversible Single-Crystal to Single-Crystal Substitution Reactions at Mn(II) Centers by Nitrile Guest Molecules. *J. Am. Chem. Soc.* **2009**, 131, 10942-10949.
19. Das, M.C.; Bharadwaj, P. K. Effect of Bulkiness on Reversible Substitution Reaction at MnII Center with Concomitant Movement of the Lattice DMF: Observation through Single-Crystal to Single-Crystal Fashion. *Chem. Eur. J.***2010**, 16, 5070-5077
20. Wang, Y.; Liu, G. X. Synthesis, Crystal Structure and Photoluminescent Properties of A Novel N,O-bifunctional Schiff-Base and Its Cadmium(II) Complex. *Chinese J. Inorg. Chem.* **2009**, 25, 713-719.
21. Sheldrick, G. M. *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, Göttingen, Germany **1997**.
22. Sheldrick, G. M. *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, **1997**.
23. Wang, R. H.; Gong, Y. Q.; Han, Lei; Yuan, D. Q.; Hong, M. C. From Chain to Layer Structure: Zn^{II} Coordination Polymers Derived from Diphenic Acid. *Chinese J. Struct. Chem.* **2005**, 24, 1007-1016.
24. Li, X. F.; Liu, Q. Y.; Xie, Z. L.; Li, T. H.; Li, Y. F.; Cao, R. Conformation Diversity of Complexes Constructed by N-(2-Pyridylmethyl)-phenylalanine and Zn(II). *Chinese J. Struct. Chem.* **2009**, 28, 53-60.
25. Yam, V. W. W.; Lo, K. K. W. Luminescent Polynuclear d^{10} Metal Complexes. *Chem. Soc. Rev.* **1999**, 28, 323-334

Table 1 Summary of crystal data and structural refinements for compounds 1 and 2.

Compound	**1**	**2**
Formula	$C_{42}H_{40}N_4O_{17}Zn_2$	$C_{37}H_{31}N_5O_{10}Zn_2$
Fw	1003.52	836.41
Space group	$P2_1/c$	$P2_1/c$
a/Å	9.5164(9)	14.344(1)
b/Å	5.6425(4)	17.542(1)
c/Å	39.571(3)	13.836(1)
β/°	93.576(3)	102.309(1)
V/Å^3	2120.7(3)	3401.6(5)
Z	2	4

D_c/g•cm^{-3}	1.572	1.633
μ(Mo-Kα)/mm^{-1}	1.213	1.480
Goodness-of-fit on F^2	1.017	1.033
F(000)	1032	1712
2θ range (°)	3.07-26.00	1.86-26.00
Reflections collected	11242	17301
Independent, observed reflections (*R*int)	3977, 1674(0.1196)	6658, 5617(0.0218)
Largest and Mean Δ/σ	0.000/0.000	0.001/0.000
Δρ (max/min) (e/ Å^3)	0.822/-0.839	1.114/-0.729
*R*1, *wR*2 [$I>2\sigma(I)$]	0.0846/0.2135	0.0395/0.1107
*R*1, *wR*2 (all data)	0.1939/0.3148	0.0477/0.1177

$R1 = \sum||F_o| - |F_c|| / \sum|F_o|$, $wR2 = \{\sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2\}^{1/2}$

Table 2. Selected bond lengths [Å] for compounds **1** and **2**.

Compound **1**					
Zn(1)-O(4)#1	1.904(7)	Zn(1)-O(5)	1.938(8)	Zn(1)-O(1W)	2.006(7)
Zn(1)-N(2)	2.006(8)				
Hydrogen bond					
O1W...O6#2	2.675(9)	O1W...O2#3	2.713(10)		
Compound **2**					
Zn(1)-O(2)	2.0257(19)	Zn(1)-O(8)	2.059(2)	Zn(1)-O(6)#4	2.125(2)
Zn(1)-N(5)	2.130(2)	Zn(1)-N(4)	2.168(2)	Zn(1)-O(5)#4	2.360(2)
Zn(2)-O(4)#5	1.965(2)	Zn(2)-O(1W)	2.056(2)	Zn(2)-N(3)	2.117(2)
Zn(2)-O(7)	2.141(2)	Zn(2)-N(2)	2.147(2)	Zn(2)-O(8)	2.469(2)
Hydrogen bond					
O2W...O3#6	2.746(3)	O2W...O7#7	2.833(3)		

Symmetry transformations used to generate equivalent atoms: #1: x-1, y, z; #2: x, y-1, z; #3: -x+1, -y-1, -z; #4: 1-x, y-0.5, 0.5-z; #4: -x, y-0.5, 0.5-z; #6: -x, -y-1, -z; #7: -x, 1.5 -y, 0.5+z.

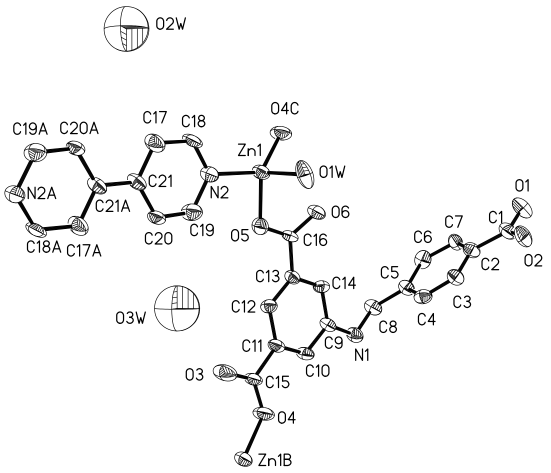

Fig. 1 Asymmetric unit of compound **1** drawn at 30% probability thermal ellipsoids. Hydrogen atoms were omitted for clarity. Symmetry codes for the generated atoms: A, 1-x, -y, -z; B, 1+x, y, z; C, x-1, y, z.

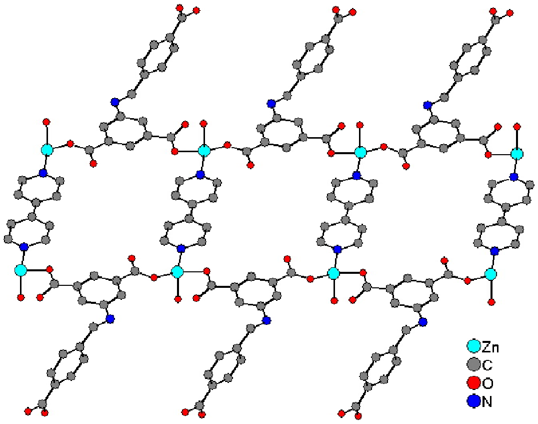

Fig. 2 The double chain structure of compound **1**. Hydrogen atoms and lattice water molecules were omitted for clarity

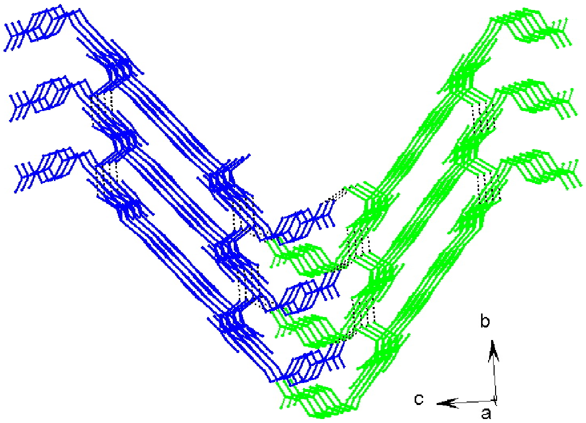

Fig. 3 View of the structure of compound **1** down the a-axis. Hydrogen atoms and lattice water molecules were omitted for clarity. The hydrogen bonds are represented by the black dashed lines.

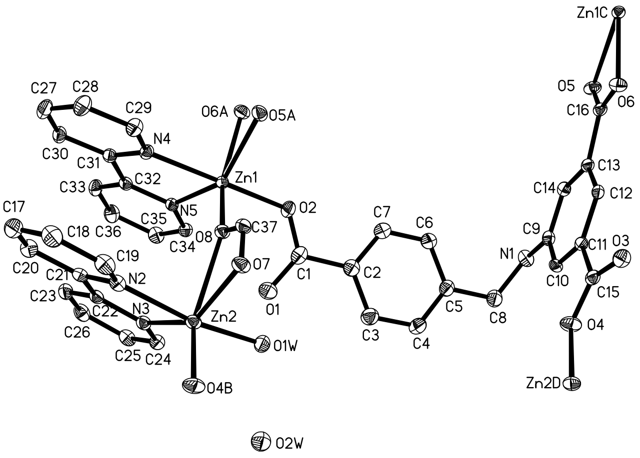

Fig. 4 Asymmetric unit of compound **2** drawn at 30% probability thermal ellipsoids. Hydrogen atoms were omitted for clarity. Symmetry codes for the generated atoms: A, -x, y-0.5, 0.5-z; B, 1-x, y-0.5, 0.5-z; C, 1-x, 0.5+y, 0.5-z; D, -x, 0.5+y, 0.5-z.

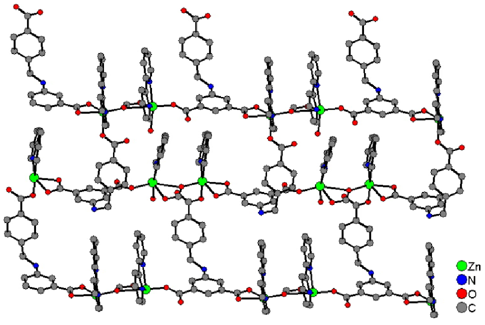

Fig. 5 The layer structure of compound **2**. Hydrogen atoms and lattice water molecules were omitted for clarity

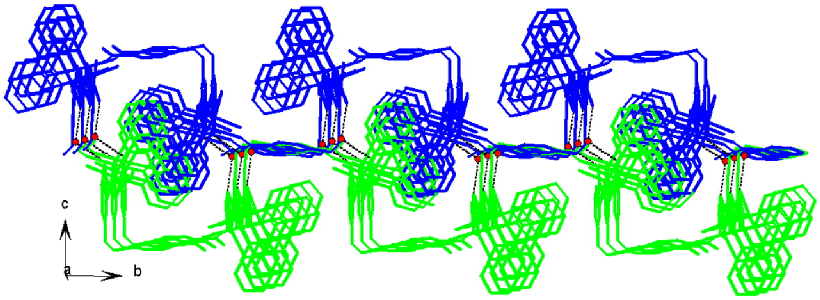

Fig. 6 View of the structure of compound **2** down the a-axis. Hydrogen atoms were omitted for clarity. The lattice water molecules are represented by the red ball. The hydrogen bonds are represented by the black dashed lines

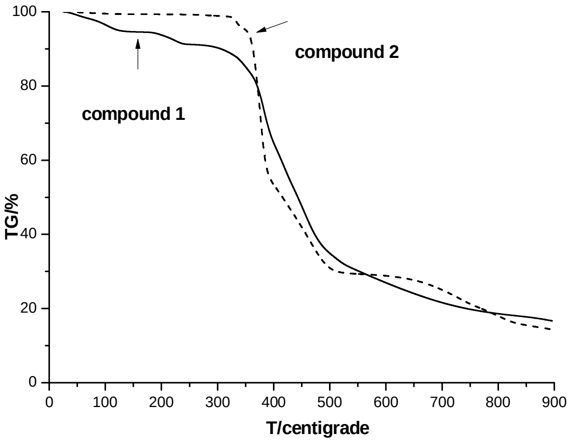

Fig. 7 The TGA curve of compounds **1** and **2**

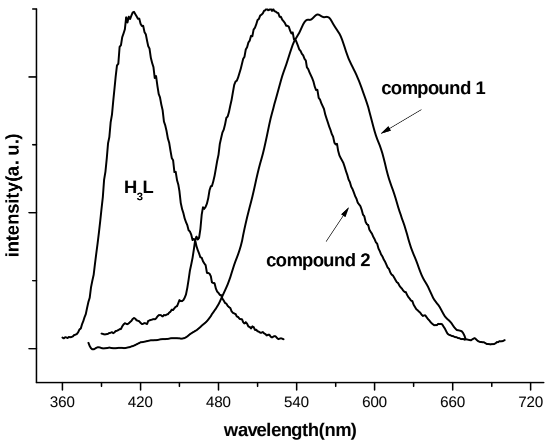

Fig. 8 The solid-state luminescent emission spectrum of compounds **1, 2** and H_3L.