Syntheses, crystal structures, and characterization of four homochiral coordination polymers based on two chiral reduced Schiff base ligands

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Abstract Four homochiral coordination polymers incorporating two chiral reduced Schiff base ligands, namely, $[Cu(L^1)(H_2O)] \cdot H_2O$ (1), $[Zn_2(L^2)_2]$ (2), $[Co(L^2)(H_2O)]$ (3), and $[Ni(L^2)(H_2O)]$ (4) $(H_2L^1 = N-(4-carboxyl)benzyl-L-alanine, H_2L^2 = N-(4-carboxyl)benzyl-L-leucine) have been obtained by hydrothermal methods and characterized by physico-chemical and spectroscopic methods. X-ray crystallographic analysis reveals that complex 1 exhibits a chain structure with 1D channels. Complexes 2–4 all are 3D network structures with 1D channels in which the isobutyl group of the ligand points toward to the channel. Complex 2 displays strong photoluminescent emission in the purple region.$

Introduction

In recent years, functional coordination complexes have received much attention because of their potential applications in fields such as catalysis, ion exchange, intercalation chemistry, photochemistry, selective separation, physical, and materials chemistry [1–9]. Such complexes can be divided into two categories according to the space group, namely, centrosymmetric complexes or noncentrosymmetric (NCS) complexes. NCS complexes are of great interest because of their potential applications in areas such as pyroelectricity, ferroelectricity, and especially second-order

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S.-M. Ying (⊠) · X.-H. Huang Department of Chemistry, Ningde Normal University, Ningde 352100, People's Republic of China e-mail: yingshaoming@126.com nonlinear optical (NLO) materials [10–17]. Compared with centrosymmetric complexes, NCS complexes are hard to obtained because the inorganic-organic hybrid systems normally tend to arrange in opposite directions to give centrosymmetric structures. Several approaches have been developed to resolve this problem: These include the introduction of Jahn–Teller-distorted cations (such as Ti^{4+} , Nb^{5+} , W^{6+}) or lone-pair cations (such as Pb²⁺), the uses of chiral or asymmetric ligands and the introduction of polar guest molecules into the system [18]. To induce NCS structures, the use of the chiral ligands is a convenient and efficient method [19]. For this purpose, we have studied reduced Schiff base ligands incorporating a chiral carbon atom. Such reduced Schiff base ligands can be obtained by reaching amino acids which have a chiral carbon atom with 4-carboxybenzaldehyde to provide the corresponding Schiff bases, then reducing the C=N bond. To data, to the best of our knowledge, examples of NCS complexes based on reduced Schiff base ligands of this type are still rare [20, 21]. In order to extend these studies, we have synthesized two chiral reduced Schiff base ligands by the reactions of 4-carboxybenzaldehyde with L-alanine or L-leucine, and four NCS complexes have been obtained. Herein, we report their syntheses, characterization, and crystal structures.

Experimental

Materials and instruments

All the chemicals were obtained from commercial sources and used without further purification. H_2L^1 and H_2L^2 were synthesized according to the procedures previously described [21–23]. C, H, and N elemental analyses were performed on a German Elementary Vario EL III instrument. FTIR spectra were recorded on a Perkin-Elmer Spectrum 2000 spectrometer using KBr pellets in the range of 4,000–400 cm⁻¹. Thermogravimetric analyses were carried out on a NETZSCH STA 449C unit at a heating rate of 10 °C/min under a nitrogen atmosphere from room temperature to 900 °C. Powder X-ray diffraction (PXRD) data were collected on a Bruker D8 Advance instrument using Cu–K α radiation ($\lambda = 1.54056$ Å) at room temperature. Photoluminescence spectra were collected on an Edinburgh FLS920 spectrometer equipped with a continuous Xe900 Xenon lamp at room temperature.

Synthesis of $[Cu(L^1)(H_2O)] \cdot H_2O$ (1)

To a mixture of Cu(NO₃)₂·3H₂O (48 mg, ca. 0.2 mmol), H₂L¹ (43 mg, ca. 0.2 mmol), EtOH (6 mL), and deionized water (6 mL) were slowly added 1 M NaOH solution drop by drop with stirring until the suspension changed to a transparent solution. The mixture was then filtered, and the filtrate was kept at room temperature. After about 2 weeks, blue block crystals of complex **1** were obtained in ca. 50 % yield based on H₂L¹. Elemental analyses for **1**, C₁₁H₁₅CuNO₆ (320.78): C, 41.3; H, 4.3; N, 4.4 %; Calcd.: C, 41.2; H, 4.7; N, 4.4 %. IR (KBr pellet, cm⁻¹): 3,217(s), 1,614(s), 1,556(s), 1,452(s), 1,371(s), 1,269(m), 1,184(m), 1,134(m), 1,082(s), 1,009(m), 847(m), 812(m), 771(s), 727(m).

Synthesis of $[Zn_2(L^2)_2]$ (2)

A mixture of Zn(NO₃)₂·6H₂O (0.059 g, 0.2 mmol), H₂L² (0.027 g, 0.1 mmol), DMF (1 mL), EtOH (3 mL) and deionized water (3 mL) was sealed into a steel bomb equipped with a Teflon liner (15 mL), and then heated at 90 °C for 3 days. White needle crystals of complex **2** were recovered in ca. 35 % yield based on H₂L². Elemental analyses for **2**, C₂₈H₃₄N₂O₈Zn₂ (Mr = 657.31): C, 51.2; H, 5.0; N, 4.2 %; Calcd.: C, 51.1; H, 5.2; N, 4.3 %. IR data (KBr, cm⁻¹): 3,267(s), 2,958(s), 1,672(vs), 1,616(s), 1,593(s), 1,552(s), 1,412(vs), 1,327(s), 1,252(s), 1,205(s), 1,182(m), 1,045(m), 1,094(m), 970(m), 933(m), 850(s), 771(m), 715(m).

Synthesis of $[Co(L^2)(H_2O)]$ (3)

The synthesis of complex **3** was similar to that for **2**, except that $Co(NO_3)_2 \cdot 6H_2O$ (0.058 g, 0.2 mmol) was used instead of $Zn(NO_3)_2 \cdot 6H_2O$. Pink rod crystals of complex **3** were recovered in ca. 30 % yield based on H_2L^2 . Elemental analyses for **3**, $C_{14}H_{19}CoNO_5$ (Mr = 340.23): C, 49.4; H, 5.5; N, 4.1 %; Calcd.: C, 49.4; H, 5.6; N, 4.1 %. IR data (KBr, cm⁻¹): 3,327(s), 2,953(s), 1,609(vs), 1,564(s), 1,366(vs), 1,209(s),

1,175(vs), 1,103(m), 1,080(m), 1,038(m), 1,018(m), 930(s), 893(s), 864(m), 775(m), 710(m).

Synthesis of $[Ni(L^2)(H_2O)]$ (4)

The synthesis of complex **4** was similar to that for **2**, except that Ni(NO₃)₂·6H₂O (0.058 g, 0.2 mmol) was used instead of Zn(NO₃)₂·6H₂O. Green rod crystals of complex **3** were recovered in ca. 30 % yield based on H₂L². Elemental analyses for **4**, C₁₄H₁₉NNiO₅ (Mr = 340.01): C, 49.4; H, 5.5; N, 4.1 %; Calcd.: C, 49.4; H, 5.6; N, 4.1 %. IR data (KBr, cm⁻¹): 3,326(m), 2,951(m), 1,605(vs), 1,562(s), 1,403(s), 1,369(s), 1,208(m), 1,175(m), 1,139(m), 1,102(m), 1,038(m), 1,019(m), 933(m), 902(m), 863(m), 847(m), 769(m), 712(m).

X-ray analysis

Data collections for complexes 1-4 were performed on a Bruker Smart Apex CCD diffractometer equipped with a graphite monochromated Mo–K α radiation ($\lambda = 0.71073$ Å). Intensity data for the four complexes were collected using ω scans at 173 K. The data sets were corrected for Lorentz and polarization factors as well as for absorption using the SAD-ABS program. All structures were solved by direct methods and refined by full-matrix least-squares fitting on F^2 by SHELX-97 [24]. All nonhydrogen atoms were refined with anisotropic thermal parameters, whereas all hydrogen atoms were generated geometrically and refined isotropically. Atoms C26, C27, and C28 which comprise the isobutyl group in complex 2 were twofold disordered, and therefore refined in two positions. Crystallographic data and structural refinements are summarized in Table 1. Selected bond lengths are listed in Table 2.

Results and discussion

As shown in Fig. 1, complex 1 contains one Cu(II) atom, an anionic L^1 ligand, a coordinated water ligand and a lattice water molecule in its asymmetric unit. The Cu(II) atoms are four-coordinated by two oxygen atoms and a nitrogen atom from two L ligands, and a water ligand in a distorted tetrahedral geometry. The Cu–O distances range from 1.917(3) to 1.940(3) Å, while the Cu–N distance is 2.013(3) Å, which are comparable to the values reported for other Cu(II) complexes [25]. The L¹ chelates a Cu(II) atom by means of a nitrogen atom and an oxygen atom of the carboxyl group and also bridges with an other Cu(II) atom. By means of these bridging ligands, a 1D left-hand helical chain is formed (Fig. 2). These chains are further linked by hydrogen bonds between the water molecules

Table 1 Summary of crystal data and structural refinements for complexes 1-4

Complex	1	2	3	4
Empirical formula	C ₁₁ H ₁₅ CuNO ₆	$C_{28}H_{34}N_2O_8Zn_2$	C14H19CoNO5	C14H19NNiO5
Formula weight	320.78	657.31	340.23	340.01
Crystal system	Tetragonal	Orthorhombic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 4 ₃	P21212	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$
a(Å)	7.5156(6)	21.1766(18)	5.9014(3)	5.795(3)
$b(\text{\AA})$	7.5156(6)	22.4239(19)	11.8762(6)	11.807(6)
$c(\text{\AA})$	22.679(3)	6.5093(6)	22.0534(11)	21.974(10)
$V(\text{\AA}^3)$	1281.0(2)	3091.0(5)	1545.64(13)	1503.4(13)
Ζ	4	4	4	4
$D_c ({\rm g}{\rm cm}^{-3})$	1.663	1.412	1.462	1.502
μ (Mo–K α) (mm ⁻¹)	1.727	1.600	1.130	1.310
<i>F</i> (000)	660	1,360	708	712
Measured-reflections	6,614	11,927	6,719	6,806
Unique-reflections [R _{int}]	2,475(0.0601)	5,723(0.0715)	2,437(0.0445)	2,434(0.0849)
GOF on F^2	1.032	1.010	1.181	0.0856
hkl range	$-6 \le h \le 9$	$-25 \le h \le 24$	$-7 \le h \le 7$	$-7 \le h \le 6$
	$-9 \le k \le 9$	$-27 \le k \le 27$	$-14 \le k \le 14$	$-14 \le k \le 14$
	$-27 \le l \le 26$	$-8 \le l \le 2$	$-25 \le l \le 18$	$-25 \le l \le 24$
<i>R</i> 1, <i>wR</i> 2 [$I > 2\sigma(I)$]	0.0414/0.1091	0.0552/0.1227	0.0432/0.1194	0.0485/0.0758
R1, wR2 (all data)	0.0416/0.1096	0.0767/0.1381	0.0675/0.1626	0.0738/0.0849
Flack parameter	-0.005(16)	0.02(3)	-0.04(4)	0.00(2)

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

Table 2 Selected bond lengths (Å) for 1-4

Complex 1					
Cu(1)-O(2W)	1.917(3)	Cu(1)-O(3)#1	1.925(3)	Cu(1)–O(2)	1.940(3)
Cu(1)-N(1)#1	2.013(3)				
Complex 2					
Zn(1)-O(1)#2	1.960(5)	Zn(1)–O(3)	1.980(4)	Zn(1)-O(5)#3	2.003(4)
Zn(1)–O(7)	2.092(4)	Zn(1)-N(2)#3	2.240(4)	Zn(2)–O(8)	1.941(4)
Zn(2)-O(5)#3	1.987(4)	Zn(2)-O(3)#4	2.007(4)	Zn(2)-O(2)#5	2.040(5)
Zn(2)-N(1)#4	2.243(5)				
Complex 3					
Co(1)–O(2)	2.069(5)	Co(1)-O(3)#6	2.084(5)	Co(1)–O(4)#7	2.094(4)
Co(1)–O(1 W)	2.088(5)	Co(1)–O(4)#8	2.164(4)	Co(1)-N(1)#8	2.213(6)
Complex 4					
Ni(1)-O(1)#9	2.029(4)	Ni(1)–O(4)	2.043(4)	Ni(1)-O(2)#10	2.049(3)
Ni(1)-O(1W)	2.057(3)	Ni(1)-O(2)#11	2.115(3)	Ni(1)-N(1)#11	2.159(4)

Symmetry transformations used to generate equivalent atoms: #1 y - 1, -x + 1, z + 1/4, #2 x - 1/2, -y + 3/2, -z + 4, #3 -x + 1/2, y - 1/2, -z + 3, #4 x, y, z - 1, #5 x - 1/2, -y + 3/2, -z + 3, #6 -x + 1, y - 1/2, -z + 1/2, #7 -x + 3/2, -y + 2, z - 1/2, #8 -x + 2, y - 1/2, -z + 1/2, #9 -x + 2, y - 1/2, -z + 3/2, #10 -x + 3/2, -y + 1, z + 1/2, #11 -x + 1, y - 1/2, -z + 3/2

and the oxygen atoms of the ligands into a supramolecular structure (Fig. 3).

Complex 2 contains two Zn(II) atoms and two anionic L^2 ligands in its asymmetric unit (Fig. 4). The Zn(II) atoms all are five-coordinated by four oxygen atoms and a

nitrogen atom from four L ligands in a distorted trigonal bipyramid geometry. The Zn–O distances range from 1.960(5) to 2.092(4) Å, while the Zn–N distances are 2.240(4) and 2.243(5) Å, which are comparable to values reported for other Zn(II) complexes [26]. The coordination



Fig. 1 The molecular structure of complex 1 with 30 % probability displacement *ellipsoids*. Hydrogen atoms were omitted for clarity. Symmetry codes for the generated atoms. A y - 1, 1 - x, 0.25 + z, B 1 - y, 1 + x, z - 0.25

modes of the two L^2 ligands are of the same. Each bridges and chelates four Zn(II) atoms. Furthermore, the Zn(II) atoms are bridged by one carboxyl oxygen of the L^2 ligand to form a 1D chain, which is further coupled by the phenyl carboxylate groups of the neighboring L^2 ligands to propagate into a 3D framework structure (Fig. 5). The 3D framework contains two kinds of cavities that are occupied by the isobutyl groups.

Complexes 3 and 4 are isostructural and also exhibit a 3D structure. The structure of 3 will be discussed in detail as an example. As shown in Fig. 6, complex 3 contains one Co(II) atom, an anionic L² ligand, and a coordinated water ligand in its asymmetric unit. The Co(II) atom is sixcoordinated by four oxygen atoms and a nitrogen atom from four L² ligands and an oxygen atom from the water ligand. The Co-O distances ranges from 2.069(5) to 2.164(4) Å, and the Co-N distance is 2.213(6), which are again comparable to values reported for other Co(II) complexes [25]. Each L^2 ligand chelates a Co(II) atom and also bridges with three other Co(II) atoms. The Co(II) atoms are bridged by the L² ligands to a form 3D framework structure with a 1D chain (Fig. 7). The 3D framework contains two kinds of cavities that are occupied by the isobutyl groups.

The simulated and experimental PXRD patterns of complexes 1–4 are in good agreement (see ESI, Figs. S1–S4), indicating the phase purity of the products. The thermal behavior of complexes 1–4 was also studied, and



Fig. 3 View the structure of complex 1 down the c axis. The hydrogen bonds are represented by *dashed lines*

the thermal curves are given in the ESI Figs. S5-S8. The TGA curve of complex 1 exhibit two stages of weight loss. The first stage is assigned to the release of the lattice water molecules (from 40 to 75 °C, expt.: 5.4 %, calcd.: 5.6 %); the second stage arises from release of the water ligands followed by decomposition of the organic ligands (from 190 to 440 °C). The TGA curve of complex 2 shows that it is stable until 390 °C; the decomposition temperature of this complex spans the range of 390-470 °C. According to the TGA curve of complex 3, the water molecules are lost in the range of 115-150 °C, expt.: 5.0 %, calcd.: 5.3 %; the decomposition temperature of this complex is in the range of 360-490 °C. Finally, the TGA curve of 4 shows that the water molecules are lost in the range of 140-180 °C, expt.: 5.2 %, calcd.: 5.3 %, and the decomposition temperature of this complex is in the range of 360-450 °C.

The solid-state photoluminescence spectrum of complex **2** at room temperature is depicted in Fig. 8. Complex **2** exhibits emission peaks at 414 nm upon excitation at 302 nm. The emission bands of complex **2** most likely originate from intraligand luminescent emissions [27].



Fig. 2 The structure of the chain in complex 1



Fig. 4 The molecular structure of complex **2** with 30 % probability displacement *ellipsoids*. Hydrogen atoms were omitted for clarity. Symmetry codes for the generated atoms. A 1.5 - x, 0.5 + y, -z-1, B 0.5 + x, 0.5 - y, -z-2, C 0.5 + x, 0.5 - y, -1-z, D x, y, z + 1, E x - 0.5, 0.5 - y, -z-2, F x - 0.5, 0.5 - y, -z-1, G x, y, z - 1, H 1.5 - x, y - 0.5, -z-1



Fig. 5 View of the structure of complex 2 down the *c* axis. Hydrogen atoms were omitted for clarity

Conclusion

In summary, we have synthesized four homochiral coordination polymers based on the chiral N-(4-carboxyl) benzyl-L-alanine or the N-(4-carboxyl)benzyl-L-leucine ligands. This example illustrates that NCS complexes can be relatively easily obtained by the use of chiral ligands. In our future work, we will concentrate our efforts on



Fig. 6 The molecular structure of complex **3** with 30 % probability displacement *ellipsoids*. Hydrogen atoms were omitted for clarity. Symmetry codes for the generated atoms. A 2 - x, -0.5 + y, 0.5 - z, B 1.5 - x, 2 - y, z - 0.5, C 1 - x, y - 0.5, 0.5 - z, D 1 - x, y + 0.5, 0.5 - z, E 1.5 - x, 2 - y, z + 0.5, F 2 - x, 0.5 + y, 0.5 - z



Fig. 7 View of the structure of complex 3 down the *a* axis. Hydrogen atoms were omitted for clarity



Fig. 8 The solid-state photoluminescent spectra of complex 2

construction of the NCS complexes for potential applications in areas such as pyroelectricity, ferroelectricity, and especially second-order nonlinear optics.

Supplementary material

CCDC 902678 to 902681 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: (internet.) C44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk]. Electronic supplementary information (ESI) available: PXRD and TGA curves of the four complexes.

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References

- Yaghi OM, O'Keeffe M, Ockwig NW, Chae HK, Eddaoudi M, Kim J (2003) Nature 423:705
- 2. Kitagawa S, Kitaura R, Noro SI (2004) Angew Chem Int Ed 43:2334
- Zhao D, Timmons DJ, Yuan DQ, Zhou HC (2011) Acc Chem Res 44:123
- 4. Jiang HL, Xu Q (2011) Chem Commun 47:3351
- 5. Zhang YB, Zhang WX, Feng FY, Zhang JP, Chen XM (2009) Angew Chem Int Ed 48:5287
- 6. Pramanik S, Zheng C, Zhang X, Emge TJ, Li J (2011) J Am Chem Soc 133:4153
- 7. Wang C, Lin W (2011) J Am Chem Soc 133:4232

- 8. Xu WT, Chen L, Jiang FL, Hong MC (2012) Chin J Struct Chem 31:321
- 9. Herm ZR, Swisher JA, Smit B, Krishna R, Long JR (2011) J Am Chem Soc 133:5664
- 10. Evans OR, Lin W (2002) Acc Chem Res 35:511
- 11. Jayanty S, Gangopadhyay P, Radhakrishnan TP (2002) J Mater Chem 12:2792
- 12. Prakash MJ, Radhakrishnan TP (2006) Inorg Chem 45:9758
- Guo Z, Cao R, Wang X, Li H, Yuan W, Wang G, Wu H, Li J (2009) J Am Chem Soc 131:6894
- Zhang JH, Hu CL, Xu X, Kong F, Mao JG (2011) Inorg Chem 50:1973
- Sun CF, Hu CL, Xu X, Yang BP, Mao JG (2011) J Am Chem Soc 133:5561
- 16. Wang YT, Fan HH, Wang HZ, Chen XM (2005) Inorg Chem 44:4148
- 17. Cao GJ, Fang WH, Zheng ST, Yang GY (2010) Inorg Chem Commun 13:1047
- Li JT, Cao DK, Akutagawa T, Zheng LM (2010) Dalton Trans 39:8606
- 19. Du ZY, Sun YH, Xu X, Xu GH, Xie YR (2010) Eur J Inorg Chem 4865
- 20. Yang XL, Xie MH, Zou C, Wu CD (2011) CrystEngComm 13:6422
- 21. Ying SM (2012) Inorg Chem Commun 22:82
- 22. Das MC, Bharadwaj PK (2009) J Am Chem Soc 131:10942
- 23. Das MC, Bharadwaj PK (2010) Chem Eur J 16:5070
- 24. Sheldrick GM (2008) Acta Crystallogr A64:112
- Ma X, Li DD, Tian JL, Kou YY, Yan SP (2009) Transition Met Chem 34:475
- Qin SN, Chen ZL, Liu DC, Huang WY, Liang FP (2011) Transition Met Chem 36:369
- 27. Yam VWW, Lo KKW (1999) Chem Soc Rev 28:323