NJC
Letter

Self-assembly of a snake-like blue photoluminescent coordination polymer from 4,4′-bis(imidazol-1-ylmethyl)biphenyl and zinc acetate†

Hui-Fang Zhu,[a] Wei Zhao,[a] Taka-aki Okamura,[b] Bao-Li Fei,[a] Wei-Yin Sun*[a] and Norikazu Ueyama[b]

[a] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China. E-mail: sunwy@nju.edu.cn*
[b] *Department of Macromolecular Science, Graduate School of Science, Osaka University, Toyonaka, Osaka 560-0043, Japan*

Received (in New Haven, CT, USA) 7th January 2002, Accepted 5th February 2002
First published as an Advance Article on the web 20th August 2002

A novel snake-like zinc(II) coordination polymer with blue photoluminescence, $\{[Zn(bimb)(OAc)_2]\cdot 6H_2O\}_\infty$ [bimb = 4,4′-bis-(imidazol-1-ylmethyl)biphenyl, OAc = acetate anion], was obtained by reaction of $Zn(OAc)_2\cdot 2H_2O$ with the ligand bimb. The X-ray crystal structural analysis indicates that two independent single-stranded helical chains are interwoven like two entwined snakes and held together through hydrogen bonds and π-π interactions.

Taking inspiration from the examples of biological systems, many chemists are trying to design and prepare aggregates with specified structures from molecular building blocks.[1,2] Due to structural similarities to nucleic acids, polymetallic helical complexes are of special interest and have been investigated extensively in the past decade.[3] For double and higher-order infinite helices, there are two possibilities as suggested by Sailaja and Rajasekharan.[4] One is that the strands of the helix are independent infinite chains held together through non-covalent interactions other than the coordination bond, which is analogous to the situation in DNA. The other one is that the strands of the helix are attached through coordination bonds to a column of metal atoms that form the axis of the helix. To the best of our knowledge, the reported examples of the first type are mainly silver(I) complexes in which the chains are linked by weak Ag···Ag or van der Waals interactions.[3h,3i,4] In this paper, we report an infinite double-stranded helical zinc(II) coordination polymer $\{[Zn(bimb)(OAc)_2]\cdot 6H_2O\}_\infty$, in which the strands are held together by hydrogen bonds and weak π-π interactions.

On the other hand, it has been reported that 1,4-bis(imidazol-1-ylmethyl)benzene (bix) reacted with $AgNO_3$[5] or $Zn(NO_3)_2\cdot 6H_2O$[6] to give an infinite polyrotaxane network and with $Mn(NO_2)_2$[7] to generate an infinite 1D chain. In order to investigate the influence of the bridging ligand on the formation of supramolecular complexes, we designed and synthesized a new ligand, 4,4′-bis(imidazol-1-ylmethyl)biphenyl (bimb), and have obtained a poly-metallocage complex $[Mn(bimb)_3][ClO_4]_2\cdot 2H_2O$ by reaction of the bimb ligand with $Mn(ClO_4)_2\cdot 6H_2O$.[8] The results suggest that even subtle changes in the organic ligand may have a great influence on the formation of metal-organic frameworks. Now we have extended the study of the reaction of bimb with other metal salts and obtained a novel complex with specific topology and blue photoluminescence by reaction of bimb with zinc(II) acetate.

The crystalline product was studied by thermogravimetric analysis (TGA) and luminescence measurements. The TGA results showed that all of the six water molecules per formula unit were lost below 85 °C with a weight loss of 18.0% (calcd. 17.8%). No further weight loss was observed for the dehydrated compound up to 270 °C. Zinc(II) complexes with pyridine and polypyridine ligands have been reported to show photoluminescence properties.[9,10] However, the photoluminescence of zinc(II) complexes with imidazole-containing ligands is not well-known. In our case, the complex in the form of the powder was found to exhibit intense blue photoluminescence with an emission maximum at 439 nm upon photoexcitation at 360 nm. The observed luminescence is probably attributable to intraligand transitions.[9]

X-Ray crystallographic analysis provides direct evidence for the structure of the complex. The complex crystallizes in the orthorhombic space group $C222_1$ and Fig. 1 shows the asymmetric unit of $[Zn(bimb)(OAc)_2]\cdot 6H_2O$ with the atom numbering scheme. Each zinc atom coordinates with two nitrogen atoms from two different bimb ligands and two oxygen atoms of two different acetate anions, and each bimb ligand in turn binds to two zinc atoms to form a 1D helical chain structure (Fig. 2). The coordination environment of the zinc atom can be regarded as a distorted tetrahedron, which is similar to

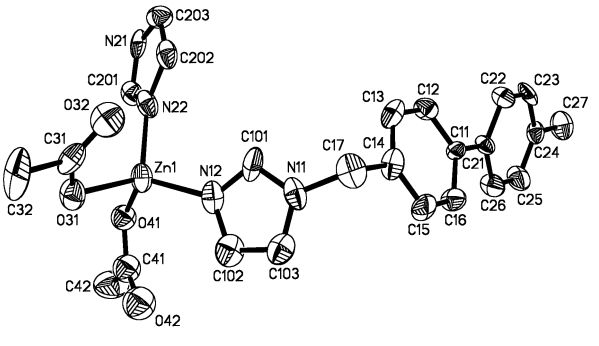

Fig. 1 Crystal structure of the asymmetric unit of $[Zn(bimb)(OAc)_2]\cdot 6H_2O$ with atom numbering scheme; hydrogen atoms and water molecules are omitted for clarity; thermal ellipsoids are drawn at 30% probability.

† Electronic supplementary information (ESI) available: color version of Fig. 3. See http://www.rsc.org/suppdata/nj/b2/b200383j/.

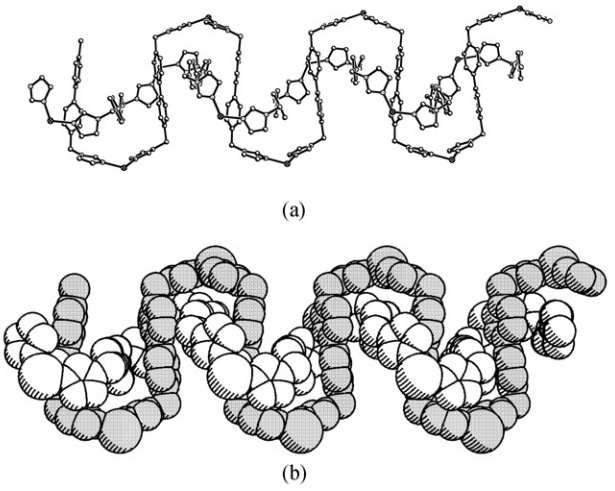

Fig. 2 (a) Perspective view of two helical chains; hydrogen atoms, acetate anions and water molecules are omitted for clarity. (b) Space-filling representation of two entwined snake-like chains.

the previously reported zinc(II) complex with the same N_2O_2 binding site.[11] The Zn–N bond lengths are 2.001(4) and 2.005(5) Å (Table 1), which are analogous to those of $[Zn(bix)_2(NO_3)_2]\cdot 4.5H_2O$ [1.994(3)–2.056(4) Å].[6] The N12–Zn1–N22 and O31–Zn1–O41 angles are 111.2(2)° and 100.7(3)°, respectively. In each bimb ligand, the dihedral angle between two terminal imidazole ring planes is 39.0° and the one between two benzene ring planes is 28.3°, which are larger than those in the reported complex of $[Mn(bimb)_3][ClO_4]_2\cdot 2H_2O$.[8] In both the Zn(II) and Mn(II) complexes, the bimb ligand has an extended geometry with a "Z" shape; namely, the two terminal imidazole groups are in opposite directions with reference to the average plane of the biphenyl group.[8]

It is noteworthy that two independent single-stranded helical chains are interwoven with each other to form a double-stranded helix [Fig. 2(a)] and it can be seen more clearly from the space-filling diagram that such a double helix looks like two entwined snakes, as illustrated in Fig. 2(b). The dihedral angle between the two strand planes defined by the zinc atoms in each strand is 49.6°. Two strands are held together by formation of C–H···O hydrogen bonds between the CH of the imidazole group from one strand and an oxygen atom of the CH_3COO^- anion from another strand with a C–O distance of 3.49 Å. In addition to the C–H···O (acetate) hydrogen bond, there are two C–H(imidazole)···O(water) bonds with C–O distances of 3.48 and 3.33 Å, three O(water)–H···O(acetate) and six O(water)–H···O(water) hydrogen bonds. Distances ranging from 2.62 to 2.92 Å between the two oxygen atoms indicate the presence of O–H···O hydrogen bonds, although the hydrogen atoms of water molecules could not be found from the experimental data. The existence of such C–H···O hydrogen bonds has been reported for histidine-containing peptides, proteins and supramolecular frameworks.[12] These hydrogen bonds link the double helix to generate a network structure (Fig. 3 and Fig. S1 in color). In addition, weak face-to-face π-π interactions are also

Table 1 Selected bond distances (Å) and angles (°) for complex $\{[Zn(bimb)(OAc)_2]\cdot 6H_2O\}_\infty$

Zn1–O31	1.972(4)	Zn1–O41	1.989(9)
Zn1–N12	2.001(4)	Zn1–N22	2.005(5)
O31–Zn1–O41	100.7(3)	O31–Zn1–N12	110.0(2)
O41–Zn1–N12	120.0(3)	O31–Zn1–N22	117.29(17)
O41–Zn1–N22	97.3(3)	N12–Zn1–N22	111.2(2)

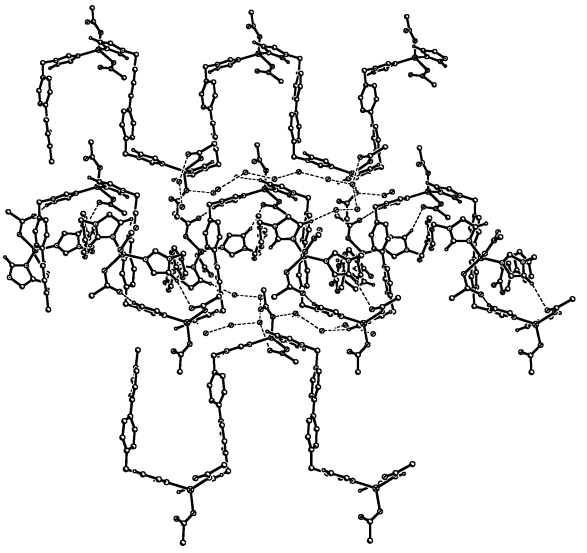

Fig. 3 Network structure of the complex linked by hydrogen bonds, indicated by dashed lines.

responsible for the formation of the double-stranded helix since the nearest center-to-center distance between two benzene ring planes of two strands is 4.17 Å with a dihedral angle of 15.9°.

Experimental

Preparation and measurements

The ligand bimb was prepared according to the literature method.[8] A solution of $Zn(OAc)_2\cdot 2H_2O$ (22.0 mg, 0.1 mmol) in water (10 ml) was added to a solution of bimb (31.4 mg, 0.1 mmol) in ethanol (10 ml) at room temperature. The mixture was stirred for 15–20 min and then filtered. The clear filtrate was allowed to stand for 4 weeks at room temperature, from which colorless needle crystals suitable for X-ray analysis were obtained. Yield: 56%. Anal. calcd for $[Zn(bimb)(OAc)_2]\cdot 6H_2O$ ($M_r = 605.94$): C 47.57, H 5.99, N 9.25; found: C 47.53, H 6.05, N 9.45; ^{1}H NMR (D_2O, 500 MHz, 298 K): δ 7.57 (s, 2H), 6.90 (s, 2H), 6.81 (s, 8H), 6.72 (s, 2H), 4.89 (s, 4H), 1.83(s, 6H).

Thermogravimetric analysis (TGA) of the crystalline sample was carried out on a simultaneous SDT 2960 thermal analyzer under flowing N_2 with a heating rate of 10 °C·min^{-1} in the 20–600 °C temperature range. Luminescence spectra were recorded on a Hitachi 850 fluorescence spectrophotometer at room temperature (25 °C).

X-Ray crystallography

A crystal of $\{[Zn(bimb)(OAc)_2]\cdot 6H_2O\}_\infty$ with approximate dimensions $0.25 \times 0.10 \times 0.05$ mm was mounted and data collection was carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer at 200 K, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). The structure was solved by direct methods using SIR92[13] and expanded using Fourier techniques.[14] All data were refined anisotropically by the full-matrix least-squares method for non-hydrogen atoms. The hydrogen atoms, except for those of the water molecules, were generated geometrically. The atoms C41, O41, O42 are disordered and have two positions with site occupancy factors (SOF) of 0.646(8) and 0.354(8). All calculations were carried out on an SGI workstation using the teXsan crystallographic software package.[15] Details of the crystal parameters, data

Table 2 Summary of crystal data and refinement results for the complex $\{[Zn(bimb)(OAc)_2]\cdot 6H_2O\}_\infty$

Empirical formula	$C_{24}H_{36}N_4ZnO_{10}$
Formula weight	605.94
Crystal system	Orthorhombic
Space group	$C222_1$
a/Å	17.6000(8)
b/Å	23.0061(11)
c/Å	14.9063(6)
U/Å^3	6034.5(5)
Z	8
T/K	200
μ/mm^{-1}	0.870
Measured reflections	6893
Observed reflections	1744
R_{int}	0.071
$R\ [I > 2\sigma(I)]$	0.0429
$wR\ [I > 2\sigma(I)]^a$	0.0484

^{a} $w = 1/[\sigma^2(F_0)^2 + (0.0068P)^2]$, $P = (F_0^2 + 2F_c^2)/3$.

collection and refinement for the compound are summarized in Table 2.

CCDC reference number 191361. See http://www.rsc.org/suppdata/nj/b2/b200383j/.

Acknowledgements

The authors are grateful to the National Nature Science Foundation of China for financial support of this work.

References

1 C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005.
2 (*a*) J. P. Sauvage, *Acc. Chem. Res.*, 1998, **31**, 611; (*b*) M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke and O. M. Yaghi, *J. Solid State Chem.*, 2000, **152**, 3; (*c*) P. Gangopadhyay and T. P. Radhakrishnan, *Angew. Chem., Int. Ed.*, 2001, **40**, 2451; (*d*) S. Y. Jon, J. Kim, M. Kim, S. H. Park, W. S. Jeon, J. Heo and K. Kim, *Angew. Chem., Int. Ed.*, 2001, **40**, 2116; (*e*) L. Carlucci, G. Ciani, D. M. Proserpio and S. Rizzato, *Chem. Commun.*, 2001, 1198; (*f*) I. Boldog, E. B. Rusanov, A. N. Chernega, J. Sieler and K. V. Domasevitch, *J. Chem. Soc., Dalton Trans.*, 2001, 893.
3 (*a*) D. Whang, J. Heo, C. A. Kim and K. Kim, *Chem. Commun.*, 1997, 2361; (*b*) L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Inorg. Chem.*, 1998, **37**, 5941; (*c*) T. Ezuhara, K. Endo and Y. Aoyama, *J. Am. Chem. Soc.*, 1999, **121**, 3279; (*d*) A. J. Blake, N. R. Champness, A. N. Khlobystov, S. Parsons and M. Schröder, *Angew. Chem., Int. Ed.*, 2000, **39**, 2317; (*e*) O. S. Jung, Y. J. Kim, Y. A. Lee, J. K. Park and H. K. Chae, *J. Am. Chem. Soc.*, 2000, **122**, 9921; (*f*) W. W. Ellis, M. Schmitz, A. A. Arif and P. J. Stang, *Inorg. Chem.*, 2000, **39**, 2547; (*g*) O. S. Jung, Y. J. Kim, Y. A. Lee, H. K. Chae, H. G. Jang and J. Hong, *Inorg. Chem.*, 2001, **40**, 2105; (*h*) L. Carlucci, G. Ciani, D. W. v. Gudenberg and D. M. Proserpio, *Inorg. Chem.*, 1997, **36**, 3812; (*i*) O. Mamula, A. von Zelewsky, T. Bark and G. Bernardinelli, *Angew. Chem., Int. Ed.*, 1999, **38**, 2945.
4 S. Sailaja and M. V. Rajasekharan, *Inorg. Chem.*, 2000, **39**, 4586.
5 B. F. Hoskins, R. Robson and D. A. Slizys, *J. Am. Chem. Soc.*, 1997, **119**, 2952.
6 B. F. Hoskins, R. Robson and D. A. Slizys, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2336.
7 H. Y. Shen, D. Z. Liao, Z. H. Jiang, S. P. Yan, G. L. Wang, X. K. Yao and H. G. Wang, *Acta Chem. Scand.*, 1999, **53**, 387.
8 B. L. Fei, W. Y. Sun, Y. A. Zhang, K. B. Yu and W. X. Tang, *J. Chem. Soc., Dalton Trans.*, 2000, 2345.
9 (*a*) N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenou, E. A. Plummer, K. Rissanen and P. Saarenketo, *J. Chem. Soc., Dalton Trans.*, 2000, 1447; (*b*) K.-Y. Ho, W.-Y. Yu, K.-K. Cheung and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1999, 1581.
10 J. Tao, M. L. Tong, J. X. Shi, X. M. Chen and S. W. Ng, *Chem. Commun.*, 2000, 2043.
11 H. K. Liu, W. Y. Sun, D. J. Ma, K. B. Yu and W. X. Tang, *Chem. Commun.*, 2000, 591.
12 (*a*) G. R. Desiraju, *Acc. Chem. Res.*, 1996, **29**, 441; (*b*) T. Steiner, *Acta Crystallogr. Sect. D*, 1995, **51**, 93.
13 A. Altomare, M. C. Burla, M. Cascarano, C. Giacovazzo, A. Guagliardi and G. Polidori, *J. Appl. Crystallogr.*, 1994, **27**, 435.
14 P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, R. de Gelder, R. Israel and J. M. M. Smits, *The DIRDIF-94 Program System*, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1994.
15 teXsan, Crystal Structure Analysis Package, Molecular Structure Corporation, The Woodlands, TX, USA, 1999.