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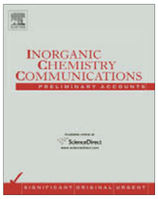

A tubular luminescent Zn(II) coordination polymer with unsymmetrical bridge ligand

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ABSTRACT

A novel 1D tubular coordination polymer $[ZnL(dca)_2]_n$ (dca = dicyanamide, L = 2-(3-pyridylmethylthio)-5-(4-pyridyl)-1,3,4-oxadiazole) constructed by the unsymmetrical bridge ligands L spirally winding around two double-chain pillars $Zn(dca)_2$ was synthesized and characterized.

1,3,4-Oxadiazole exhibiting excellent luminous property and biological activity such as antiphlogosis and antisepsis, has drawn recent great attention in organic synthesis, medicinal chemistry and materials science [1–4]. For example, in combination of an electron transporting moiety 1,3,4-oxadiazole with a hole transporting moiety carbazole, Huang et al. created a fascinating compound 2-(4-biphenylyl)-5-(4-carbazole-9-yl)phenyl-1,3,4-oxa-diazole to design high-performance blue electroluminescent devices [4]. As for coordination chemistry, it has been a hotspot to tailor polytopic ligands based on the intentional modification of 1,3,4-oxadiazole through introducing functional groups such as mercapto, pyridyl and sulfanilamide to enforce/enhance the desired properties and coordination flexibility, and some metal-organic complexes with novel structures and properties have been reported [5–8]. However, 1,3,4-oxadiazole-containing unsymmetrical ligands and their coordination compounds are comparatively uncommon [9,10]. As well known, using unsymmetrical bridging ligands as building blocks is currently selection for assembling novel helical architectures and optical materials [11,12]. Thus we simultaneously introduce mercapto and pyridyl groups into the backbone of 1,3,4-oxadiazole, and hope that the unsymmetrical configuration, coordination variety and flexibility of the resulting multifunctional ligands are in favor of construction for aesthetic structural motifs with gracious functions. Here we wish to communicate a novel 1D tubular coordination polymer $[ZnL(dca)_2]_n$ (**1**) (L = 2-(3-pyridylmethylthio)-5-(4-pyridyl)-1,3,4-oxadiazole, dca = dicyanamide), together with its electrooptical and fluorescent properties.

Ligand L shown in Scheme 1 was synthesized *via* a nucleophilic substitution reaction of 5-(4-pyridyl)-2-mercapto-1,3,4-oxadiazole and 3-(chloromethyl)pyridine under alkaline condition [3,9,10,13]. Compound **1** was synthesized as colorless block crystals by slow evaporation of an ethanol/methanol solution of L, $Na(dca)_2$ and $Zn(NO_3)_2{\cdot}6H_2O$ [14]. IR spectra disclose characteristic absorptions of 2313, 2261 and 2186 cm^{-1} for dca and 1623, 1546 and 1459 cm^{-1} for aromatic rings in **1**. Crystallographic analysis [15] reveals that compound **1** is a discrete 1D tubular architecture extending along the *b*-axis (Fig. 1).

In the structure, each zinc(II) atom locates at a distorted octahedral environment with four nitrogen atoms from dca in the equatorial plane, and a 3-pyridyl nitrogen atom and a 4-pyridyl nitrogen atom from different L at the axial sites (Fig. 2). The bond lengths of Zn–N range from 2.065(7) to 2.234(7) Å, and among which the $Zn–N5_{dca}$ of 2.234(7) Å is slight longer compared with those in literature [16–20]. The widely used versatile ligand dca anions acting as bidentate bridges adopt an end-to-end coordination mode, and doubly link with Zn(II) metal centers to form 1D annular structures with a separation of Zn(II)···Zn(II) being 7.463 Å. The double chain is almost linear and every cycle in the chain is a 12-membered $Zn(dca)_2Zn$ ring with a flat configuration, being similar to the double dca-bridged 1D polymers [16–18]. A striking structural feature of **1** is that unsymmetrical ligands L select the double-chain $Zn(dca)_2$ as pillars, wind around two pillars through its 3-pyridyl and 4-pyridyl nitrogen atoms ligating to metal centers in different pillars, and form a 1D tubular polymer with a 2_1 axis running through the tube (Fig. 1). Half dca anions of every pillar reside in the tube, which mainly results in the

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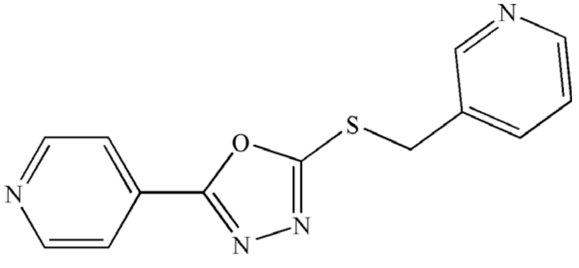

Scheme 1. Schematic representation of ligand L.

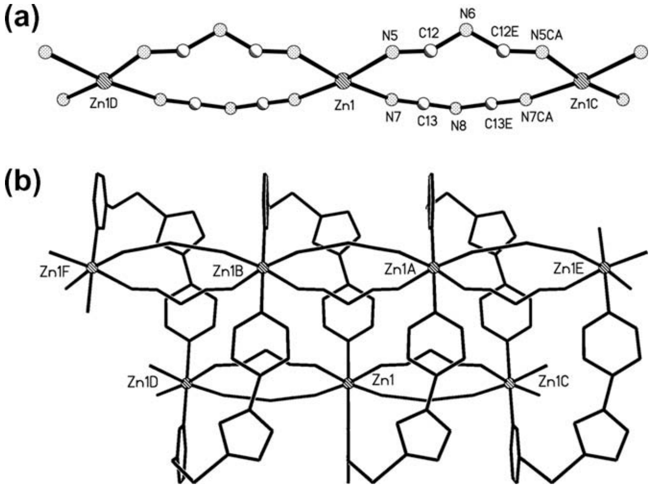

Fig. 1. (a) View of dca-bridged double-chain pillars Zn(dca) and (b) 1D tubular coordination polymer constructed by bridges L spirally winding around two double-chain pillars in **1**.

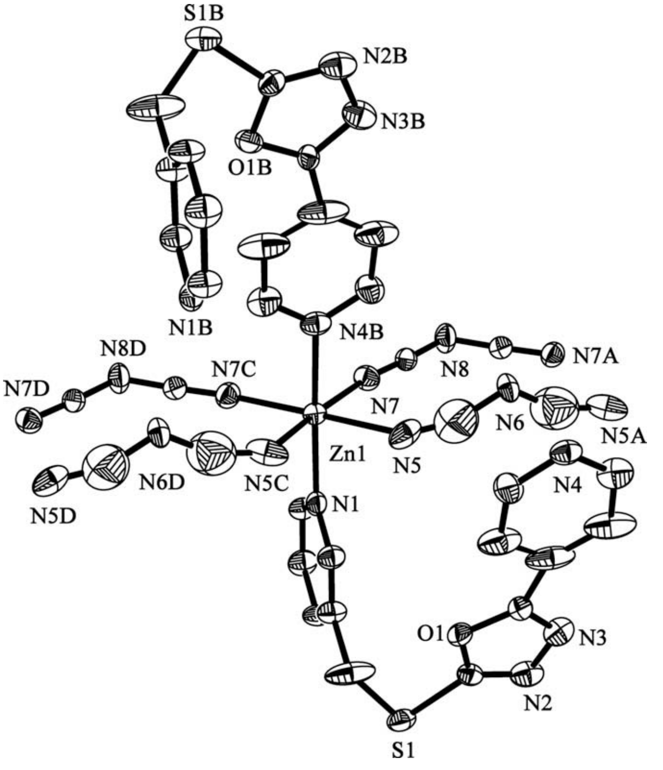

Fig. 2. Perspective view of the coordination environment of the Zn(II) ion in **1**. Selected bonds (Å) and angles (°): Zn1–N1 2.117(9), Zn1–N5 2.220(7), Zn1–N7 2.074(7), Zn1–N5C 2.220(7), Zn1–N7C 2.074(7), Zn1–N4B 2.153(9), N7–Zn1–N1 92.7(3), N7–Zn1–N5 90.3(4), N1–Zn1–N5 90.6(3), N7–Zn1–N7C 98.4(4), N7C–Zn1–N1 92.7(3), N7–Zn1–N4B 91.2(2), N1–Zn1–N4B 174.0(3), N1–Zn1–N5C 90.6(3), N7C–Zn1–N5 170.5(3), N7C–Zn1–N4B 91.2(2), N7–Zn1–N5C 170.5(3), N7C–Zn1–N5C 90.3(4), N4B–Zn1–N5C 84.8(3), N4B–Zn1–N5 84.8(3), N5C–Zn1–N5 80.8(6). A x, 1/2-y, z; B -x, y-1/2, -z; C x, -y-1/2, z; D x, y-1, z.

disorder of C12 in the half dca anions. The Zn(II)···Zn(II) distance bridged by L is 7.085 Å. Notably, every unsymmetrical ligand L allows a spiral configuration with the 4-pyridyl group being coplanar with the oxadiazole group (the dihedral angle being 6.3°) and the S-bonded 3-(methyl)pyridyl group reversely being perpendicular with the oxadiazole group (the dihedral angle being 91.5°), being obviously different from the almost flat configuration of analogue [9,10]. Especially, the thioether moiety embedded in the backbone of L not only constrains the C–S–C angle being close to 90° (96.6(5)°) but also allows the free rotation of the two bound groups along C–S bonds, thereby endowing ligand L with flexible conformations to cater for assembling requirement. Perhaps the

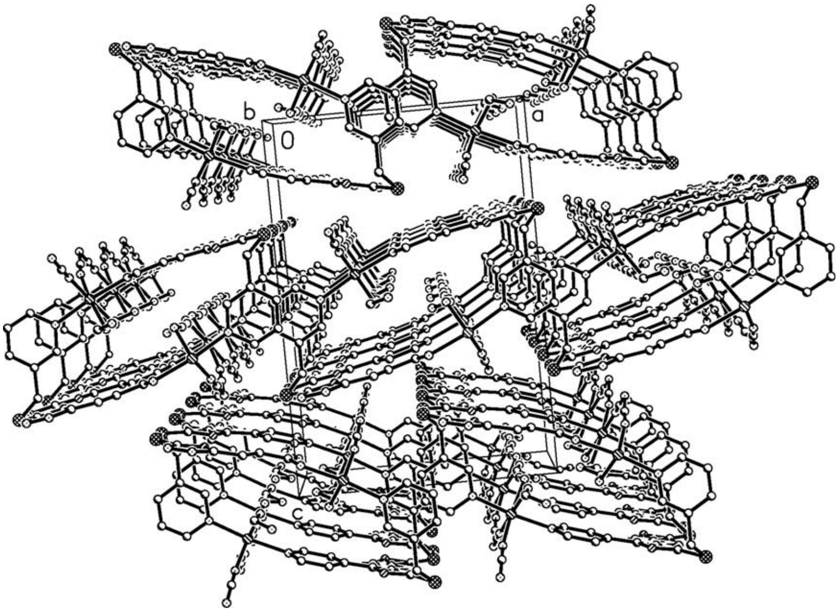

Fig. 3. View of discrete tubular polymeric units aligning in parallel along *b*-axis and complementary interchain interdigitation through the π–π stacking interactions between neighbouring tubes to result in an overall 2D sheet.

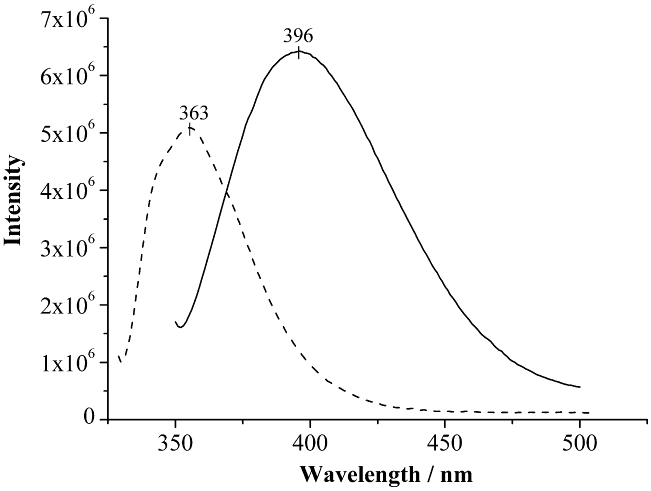

Fig. 4. Solid state photoluminescent spectra of **1** (solid line) and free ligand L (dotted line) at room temperature.

flexibility of the ligand on the thioether moiety plays an important role in the construction of the tubular structure. In a sense, complex **1** is a helical-tube polymer with a chiral void of an opening size about 14 × 6 Å^2 and a pitch of 7.463 Å, being dissimilar to the triple chain polymer containing double dca-bridged chains and the tubular polymer with the wall being similar to that of a carbon nanotube [19–21]. Although many 1D helical polymers and some 1D tubular architectures have been reported up to now, the helical-tube structure in **1** constructed by a bridge ligand spirally winding around two double-chain pillars is authentically rare [11,12,21–23].

In the crystals, all the discrete tubular polymeric units align in parallel along *b*-axis. Complementary interchain interdigitation occurs with the π–π stacking interactions between 3-pyridyl groups of the neighbouring tubes, which results in an overall 2D sheet [Fig. 3 and S1].

The electronic absorption spectra of L and **1** were respectively recorded in methanol with a concentration of 1.0 × 10^{-5} M in a 200–600 nm region using a UnicoTMUV-2102 PC UV–vis spectrometer at room temperature (Fig. S2). Two intense bands with maxima at 207 and 279 nm distinctly character L, which may be assigned to intraligand contribution of $\pi \rightarrow \pi^*$ transition. As for **1**, two stronger absorptions centered at 208 and 281 nm are slightly bathochromic in comparison with free ligand L, which mainly originates from $\pi \rightarrow \pi^*$ charge transition of L.

The photoluminescent spectra of **1** and free ligand L were measured with a Hitachi F-4500 system at room temperature. A DMF solution of L (1.0 × 10^{-4} M) excited at 308 nm emits photoluminescence with a single broad band at λ_{max} = 366 nm. When excited at 326 nm, the emission property of solid L is very similar to that of the DMF solution sample only with the maximum emission wavelength undergoing a slightly blue-shift to 362 nm. The emission of **1** in solid centers at 395 nm as excited at 343 nm (Fig. 4). Although the maximum emission wavelength of **1** undergoes a red-shift of 33 nm, the emission band is very similar to that found for free ligand L in terms of position and band shape. Therefore, the emission nature of **1** is a ligand-centered emission as reported for Zn(II) or other d^{10} metal complexes with N-donor ligands [24,25]. The intensity increase of the luminescence for **1** can be explained by the bridge coordination of L with the metal center increasing the rigidity of L and reducing the nonradiative relaxation process.

In summary, we have successfully synthesized a novel 1D tubular luminescent Zn(II) coordination polymer with the designed unsymmetrical bridge ligand L containing biologically active group 1,3,4-oxadiazole.

Supplementary material

CCDC 743772 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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References

[1] A. Talib, H. Tashtoush, K. Sasakik, Syn. Commun. 20 (1990) 1811.
[2] R.N. Vansdadia, K. Sasaki, N. Yumita, J. Inst. Chem. (India) 6 (1992) 49.
[3] D.S. Dodd, T. Nishi, United States Patent, 1997, p. 28.
[4] M. Guan, Z.Q. Bian, Y.F. Zhou, F.Y. Li, Z.J. Li, C.H. Huang, Chem. Commun. (2003) 2708.
[5] X.H. Bu, H. Liu, M. Du, L. Zhang, Y.M. Guo, M. Shionoya, J. Ribas, Inorg. Chem. 41 (2002) 1855.
[6] M. Du, X.H. Bu, Z. Huang, S.T. Chen, Y.M. Guo, C. Diaz, J. Ribas, Inorg. Chem. 42 (2003) 552.
[7] H.W. Hou, L.X. Xie, G. Li, T.Z. Ge, Y.T. Fan, Y. Zhu, New J. Chem. 28 (2004) 191.
[8] V.J. Catalano, T.J. Craig, Inorg. Chem. 42 (2003) 321.
[9] E. Ye, B.L. Wu, Y.Y. Niu, H.Y. Zhang, Synth. React. Inorg. Met.-Org. Chem. 38 (2008) 716.
[10] E. Ye, B.L. Wu, Y.Y. Niu, H.Y. Zhang, H.W. Hou, Acta Cryst. C63 (2007) m484.
[11] O.R. Evans, W. Lin, Acc. Chem. Res. 35 (2002) 511.
[12] L. Han, M. Hong, Inorg. Chem. Commun. 8 (2005) 406.
[13] R.W. Young, K.H. Wood, J. Am. Chem. Soc. 77 (1955) 400.
[14] 5-(4-Pyridyl)-2-mercapto-1,3,4-oxadiazole and ligand L were prepared as described in literature [3,9,10,13]. A solution of $Zn(NO_3)_2\cdot 6H_2O$ (0.0297 g, 0.1 mmol) in methanol (10 mL) was dropwise added into a solution of L (0.0540 g, 0.2 mmol) and Nadca (0.0178 g, 0.2 mmol) in 1:1 methanol/ethanol (20 mL) with strong stir, and then the resulting mixture was stirred at reflux temperature for 30 min and cooled down to room temperature. After filtered and allowed the filtrate to evaporate slowly at ambient temperature for one month, colorless block crystals of **1** suitable for X-ray analysis were obtained in 56% yield (based on Zn). Elemental analysis calcd (%) for $C_{17}H_{10}N_{10}OSZn$: C 43.65, H 2.15, N 29.94, S 6.85; found: C 43.61, H 2.21, N 30.12, S 6.85. Selected IR (KBr, cm^{-1}): 3424(w), 2313(m), 2261(m), 2186(s), 1623(m), 1459(m), 1383(s), 1302(m), 834(m), 701(m), 525(m).
[15] X-ray crystallography: data were collected on a Siemens Smart CCD diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 291(2) K. All absorption corrections were performed using the SADABS program. The structures was solved by direct methods and refined by full-matrix least-squares fitting on F2 by SHELXTL-97 (G.M. Shelderic, SHELXL-97, University of Göttingen, Germany, 1997). Crystal data for **1**: $C_{17}H_{10}N_{10}OSZn$, orthorhombic, space group, *Pnma*, a = 13.125(2) Å, b = 7.4625(13) Å, c = 19.057(3) Å, V = 1866.6(6) Å^3, Z = 4, D_c = 1.657 g/cm^3, ρ_{calcd} = 1.059 mm^{-1}, R_1 = 0.0860, wR_2 = 0.2184 and *GOF* = 1.031. The positions of H atoms were generated geometrically.
[16] P. Jensen, S.R. Batten, G.D. Fallon, D.C.R. Hockless, B. Moubaraki, K.S. Murray, R. Robson, J. Solid State Chem. 145 (1999) 387.
[17] I. Dasna, S. Golhen, L. Ouahab, M. Fettouhi, O. Pena, N. Daro, J.P. Sutter, Inorg. Chim. Acta 326 (2001) 37.
[18] S.C. Manna, A.K. Ghosh, J. Ribas, M.G.B. Drew, C.N. Lin, E. Zangrando, N.R. Chaudhuri, Inorg. Chim. Acta 359 (2006) 1395.
[19] J.L. Manson, A.M. Arif, C.D. Incarvito, L.M. Liable-Sands, A.L. Rheingold, J.S. Miller, J. Solid State Chem. 145 (1999) 369.
[20] (a) E.Q. Gao, S.Q. Bai, Z.M. Wang, C.H. Yan, Dalton Trans. (2003) 1759;
(b) S.R. Batten, A.R. Harris, P. Jensen, K.S. Murray, A. Ziebell, Dalton Trans. (2000) 3829.
[21] F. Chang, Z.M. Wang, H.L. Sun, S. Gao, G.H. Wen, X.X. Zhang, Dalton Trans. (2005) 2976.
[22] S. Neogi, P.K. Bharadwaj, Inorg. Chem. 44 (2005) 816.
[23] C.Y. Niu, B.L. Wu, X.F. Zheng, H.Y. Zhang, Z.J. Li, H.W. Hou, Dalton Trans. (2007) 5710.
[24] B.L. Wu, D.Q. Yuan, F.L. Jiang, R.H. Wang, L. Han, Y.F. Zhou, M.C. Hong, Eur. J. Inorg. Chem. (2004) 2695.
[25] I.V. Sazanovich, C. Kirmaier, E. Hindin, L. Yu, D.F. Bocian, J.S. Lindsey, D. Holten, J. Am. Chem. Soc. 126 (2004) 2665.