

Available online at www.sciencedirect.com



Journal of MOLECULAR STRUCTURE

Journal of Molecular Structure 873 (2008) 73-78

www.elsevier.com/locate/molstruc

1D chain Cd(II) and Co(II) coordination polymers: Synthesis, crystal structures and luminescence properties

Mei Sun ^{a,b}, Peng Wang ^a, Hongping Zhou ^{a,*}, Jiaxiang Yang ^a, Jieying Wu ^a, Yupeng Tian ^{a,c,d,*}, Xutang Tao ^c, Minhua Jiang ^c

^a Department of Chemistry, Anhui University, Hefei 230039, PR China

^b Department of Material and Chemistry, Anhui Institute of Architecture & Industry, Hefei 230022, PR China ^c State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, PR China

^d State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China

Received 6 February 2007; received in revised form 4 March 2007; accepted 4 March 2007 Available online 16 March 2007

Abstract

Two novel 1D infinite chain coordination polymers, $[CdL(NO_3)_2]_n$ and $[CoL(NO_3)_2]_n$ (L = 4,4'-bis[2-(2-pyridyl)ethenyl]biphenyl) have been prepared by reacting Cd(NO_3)_2 and Co(NO_3)_2 with the novel ligand L. Complexes 1 and 2 have been characterized by elemental analysis, IR and single crystal X-ray diffraction determination. The metal ions in the polymers have six coordinate pseudo octahedral structures with two pyridyl nitrogen atoms of L and four oxygen atoms of nitrate. The ligand coordinates to metal ions forming bridges in different geometries (*cis* and *trans* coordination modes). The results of TGA determination show that the coordination polymers are quite thermally stable. The complexes exhibit a strong emission band with the maximum intensity at 524 and 545 nm in solid-state, respectively, upon excitation at 350–450 nm.

© 2008 Published by Elsevier B.V.

Keywords: Bipyridyl ligand; Coordination polymer; Crystal structure; Fluorescence

1. Introduction

Organic/inorganic hybrid materials are currently receiving considerable attention [1–3] owing to their potential properties in magnetism, spectroscopy, catalysis, and nonlinear optical owing to their potential properties in magnetism, spectroscopy, catalysis, and nonlinear optical activity [4–7]. The hybrid materials combine the advantageous properties characteristic of crystalline inorganic solids with those of organic molecules within a molecular-scale composite. The organic compounds have low melting points or low decomposition temperatures, inhibiting their applications. The functionalized organic molecule (addition of donor atoms, e.g. N or O) allowed to incorporate into inorganic/organic coordination complexes can offer the advantages of high thermal stability and solvent resistance compared to all-organic materials.

Two components are necessary in every synthetic approach leading to extended supramolecular multimetallic assemblies: the ligand (the organic tecton) and the metal ion. In the language of supramolecular chemistry, the ligand is a programmed species, whose information is read by the metal ions according to their coordination algorithm. This is often achieved by employing bifunctional N, N'-donor ligands such as 4,4'-bipyridine or 2,2'-bipyridine and their derivatives [8–12] as linkers between adjacent metal ions. However, some organic ligands with special functionality for supramolecular architectures and functional compounds, because of synthetic difficulties, have been reported rarely to date.

On the other hand, metal ion is a key factor in determining the dimensionality of the resulting systems. A 1:1

^{*} Corresponding authors. Tel.: +86 551 5108151; fax: +86 551 5107342. *E-mail addresses:* zhpzhp@263.net (H.-P. Zhou), yptian@ahu.edu.cn (Y.-P. Tian).

^{0022-2860/\$ -} see front matter @ 2008 Published by Elsevier B.V. doi:10.1016/j.molstruc.2007.03.019

ligand-to-metal ratio leads to either linear or zig-zag chains. Metal ions also display a range of coordination geometries allowing for greater flexibility in constructing materials with specific topologies. For example, Cd(II) and Co(II)-containing coordination polymers have attracted considerable recent interest owing to the change-ability to form bonds with different donors, the large radius and various coordination modes [8,9].

Taking account of the above considerations, we have designed and synthesized a novel functional bipyridyl ligand 4,4'-bis[2-(2-pyridyl)ethenyl]biphenyl for assembling with Cd(II) and Co(II) cation. Here two novel 1D infinite chain coordination polymers, $[CdL(NO_3)_2]_n$ and $[CoL(-NO_3)_2]_n$ (L = 4,4'-bis[2-(2-pyridyl)ethenyl]biphenyl) have been prepared and structurally characterized. The compounds were characterized by single crystal X-ray crystallography.

2. Experimental

All chemicals used were of analytical grade. The solvents were purified by conventional methods.

2.1. Physical measurements

Elemental analysis data were obtained using a Perkin-Elmer 240 analyzer. Infrared spectra were recorded from KBr discs in the range 4000–400 cm⁻¹ on a Nicolet FT IR-170SX instrument. ¹H NMR spectrum was performed on Bruker 500 MHz Ultrashield spectrometer and was reported as parts per million (ppm) from TMS (δ). Electronic absorption spectra were obtained on a UV-265 spectrophotometer in DMF solution (1.0×10^{-5} mol dm⁻³). The luminescent spectra were measured on single crystals at room temperature using a model Perkin-Elmer LS55 fluorescence spectrophotometer. The excitation slit was 10 nm, the emission slit was 10 nm also, and the response time was 2 s. TGA of the compounds were carried out using a Perkin-Elmer Pris-1 DMDA-V1 analyzer in a atmosphere of N₂ at a heating rate of 20 K min⁻¹.

2.2. Synthesis

2.2.1. Preparation of the ligand (L)

4,4'-bis[2-(2-pyridyl)ethenyl] biphenyl) (L) was prepared by solid-state reaction. The mixture of biphenyl bisphosphonates (0.364 g, 1 mmol), pyridine carboxaldehyde (0.32 g, 3 mmol) and potassium *t*-butoxide was forcibly milled for 5 min. Yellow powder was collected by filtration, washed with water and ethanol and dried under vacuum. Yield: 90%. Anal. Calc. for C₂₆H₂₀N₂: C, 86.64; H, 5.59; N, 7.77. Found: C, 86.61; H, 5.63; N, 7.76%. IR (KBr, cm⁻¹): 3049 (m), 1592 (w), 1484 (w), 1435 (m), 1187 (s), 1118 (s), 997 (w), 721 (s), 541 (s). ¹H NMR (500 MHz, CDCl₃) δ 8.59 (d, J = 4.25 Hz, 2 H), 7.77–7.82 (m, 10 H), 7.73 (d, J = 16.10 Hz, 2 H), 7.58 (d, J = 7.78 Hz, 2 H), 7.39 (d, J = 16.07 Hz, 2 H), 7.26–7.28 (m, 2 H) (Fig. 1). UV–Vis (λ_{max}) /nm: 354 (π – π^*).

2.2.2. Preparation of $[CdL(NO_3)_2]_n(1)$

Crystals were obtained by using a fritted U-tube. L (0.360 g, 1 mmol) in CHCl₃ solution was placed on the side of the U-tube, and on the other side of the U-tube $Cd(NO_3)_2$ (0.948 g, 4 mmol) in ethanol was added followed by enough ethanol to equalize hydrostatic pressures on both sides. After two weeks, well-formed yellow crystals (1) were obtained within the solutions of both sides. Yield: 70%. Anal. Calc. for C₂₆H₂₀CdN₄O₆: C, 52.10; H, 3.35; N, 9.39. Found C, 52.06; H, 3.38; N, 9.42 %. IR (KBr, cm⁻¹): 821 (s), 1385 (s), 1591 (s), 3521 (s).

2.2.3. Preparation of $[CoL(NO_3)_2]_n(2)$

The complex was synthesized by the same procedure above, but from $Co(NO_3)_2$. Yield: 73%. Anal. Calc. for $C_{26}H_{20}CoN_4O_6$: C, 57.42; H, 3.68; N, 10.31. Found C, 57.45; H, 3.70; N, 10.28%. IR (KBr, cm⁻¹): 814 (s), 1278 (s), 1495 (s), 1599 (s), 3421 (s).

2.3. X-ray crystallography and structure solution

The relevant crystal data and structural parameters are summarized in Table 1. Selected bond distances and angles are shown in Table 2, respectively. Data collections $[1.77^{\circ} \leq \theta \leq 25.03^{\circ}]$ were performed using a Siemens SMART CCD area detector diffractometer with Mo Ka radiation with an ω -scan mode [$\lambda = 0.7103$ Å]. The structure was solved with direct methods using the program SHELXTL (Sheldrick, 1997) [13] and refined anisotropically with SHELXTL using full-matrix least squares procedure giving for (1) a final R_1 value of 0.0347 for 168 parameters, and 2110 unique reflections with $I \ge 2\sigma$ (I) and wR_2 of 0.0617 for all 6003 reflections, and for (2), a final R_1 value of 0.0476 for 168 parameters, and 2132 unique reflections with $I \ge 2\sigma$ (I) and wR_2 of 0.0875 for all 6284 reflections. All the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using full-matrix least-squares procedure. The hydrogen atom positions were geometrically idealized and allowed to ride on their parent atom and fixed displacement paraments.

3. Results and discussion

3.1. Syntheses

In this report, the novel ligand was first successfully synthesized by the solid-state reactions of the condensation between phosphonate ester and aldehyde derivative at room temperature. Conventionally, the reactions of the condensation between phosphonate ester and aldehyde derivatives are all prepared in a solution with a rigorous experimental condition for long reaction time in nitrogen gas and separation with column chromatography [14–17].





Table 1

Crystallographic data for ${\bf 1}$ and ${\bf 2}$

Complex	1	2
Empirical formula	C ₂₆ H ₂₀ CdN ₄ O ₆	C ₂₆ H ₂₀ CoN ₄ O ₆
Formula mass	596.86	543.39
Crystal color	Yellow	Mauve
Crystal dimensions	$0.45 \times 0.21 \times 0.13$	$0.22 \times 0.13 \times 0.11$
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2/c	C2/c
a [Å]	7.580(4)	14.530(5)
<i>b</i> [Å]	6.859(4)	13.372(5)
<i>c</i> [Å]	23.290(12)	14.267(5)
β [°]	98.041(7)	119.440(5)
V [Å ³]	1199.0(10)	2413.9(14)
Z	2	4
D_{calcd} .[g cm ⁻³]	1.653	1.495
Tot. no. data	6003	6284
No. unique data	2110	2132
R_1	0.0347	0.0476
wR_2	0.0617	0.0875
GOF	0.910	0.785

While in our approach the reactants were simply forcibly milled in open mortar at room temperature for several minutes. The method of dealing with the product is facility in washing by water and ethanol. During synthesis and dealing process, the product was obtained without any organic

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

1			
Cd(1)-N(1)	2.227(3)	N(1)-Cd(1)-N(1A)	122.98(15)
Cd(1)-N(1A)	2.227(3)	N(1)-Cd(1)-O(1)	89.36(9)
Cd(1)–O(2)	2.305(3)	N(1)-Cd(1)-O(2)	122.05(9)
Cd(1) - O(1)	2.444(2)	O(2)-Cd(1)-O(1)	53.72(9)
		O(3)–N(2)–O(1)	121.7(4)
2			
Co(1) - N(1)	2.065(3)	N(1)-Co(1)-O(1)	106.09(12)
Co(1)-N(1A)	2.065(3)	N(1)-Co(1)-O(2)	87.98(12)
Co(1)–O(1)	2.065(3)	O(1)-Co(1)-O(2)	58.02(12)
Co(1)–O(2)	2.264(3)	O(3) - N(2) - O(2)	123.4(5)
		N(1)-Co(1)-N(1A)	100.62(19)

solvent, which agrees with the principles of 'green chemistry'.

3.2. Infrared spectra

Based on IR spectra, we can deliberately diagnose the coordination mode of the nitrate group in complexes 1 and 2. Specifically, asymmetric stretching vibrations $v_{as}(N-O)$ appear near 1591 cm⁻¹ for 1 and 1599 cm⁻¹ for 2, and the symmetric stretching vibrations $v_s(N-O)$ are

observed near 1385 cm⁻¹ for 1 and between 1495 and 1278 cm⁻¹ for 2. The separations $[v_{as}(N-O)-v_s(N-O)]$ of complexes 1 and 2 (206 and 321 cm⁻¹) are much larger than the value of 180 cm⁻¹ for the free nitrate group, indicating that the coordinated nitrate group is in a bidentate bridging or chelating mode, which can be proved by their crystal structural determination. While in 2, the absorption peaks around $v_s(N-O)$ bands split and made the spectrum become more complicated. The δ_{N-O} (out-of-plane bending vibration) bands appeared at 821 and 814 cm⁻¹ for 1 and 2. This fact may be explained by the behavior of the N atom in the pyridine ring as a metal binding site.

3.3. Crystal structure of (1) and (2)

Single crystal X-ray diffraction analysis reveals that the structure of the complex 1 presents an 1-D zig-zag infinite chain as depicted in Fig. 3. The coordination geometry around the Cd(II) center in (1) is shown in Fig. 2. Cd(1) resides on a crystallographic two-fold axis and the metal centers all adopt six coordination modes. Each Cd center is coordinated by two nitrogen atoms of the two bipyridyl ligands and to four oxygen atoms of nitrate in a bidentate fashion. The overall geometry around the Cd center can be described as a pseudo octahedral. The polyhedron contains oxygen and nitrogen atoms with a maximum deviation of 0.2990 Å from the idealized plane defined by the Cd and oxygen atoms. The axially coordinated in a trans configuration with two bipyridyl ligand nitrogen atoms form a N(1)-Cd(1)-N(1A) angle of 122.98°. Bidentate



Fig. 2. Molecular structure and atom numbering of 1.

nitrate coordination is quite common for cadmium complexes [18,19] and previously characterized cadmium complexes exhibit essentially identical Cd–O bond lengths for the bidentate nitrate group. But in complex 1 the two oxygen atoms of the bidentate nitrate group bind to Cd unsymmetrically with Cd–O distances of 2.444(2) and 2.305(3) Å, respectively. The two identical Cd–N distances of 2.227(3) Å are comparable to those of known cadmium pyridine complexes [19]. Contrasting to the free ligand, the ligand is still highly planar and conjugated, leading to a π bridge for the charge transfer, which can be proved by its luminescent properties.

The chain polymer is composed of $[CdL(NO_3)_2]_n$ monomer. A compact single stranded 1-D zig-zag chain is formed by self assembly of $[CdL(NO_3)_2]_n$ via coordination of metal-related peripheral pyridine-N of this unit to the neighbouring Cd(II) center running along a crystallographic axis in the *c* direction. The adjacent chains are linked by the C-H···O to form plane. The bond length of C-H···O is 2.437 Å and the angle of C-H···O is 131.36°. The planes are similarly separated by 3.646 Å, suggesting π - π stacking interactions (Fig. 4).

In the complex 2, the Co centers also adopt six-coordination modes in Fig. 5, but they present different architectures from Cd centers, indicating that the nature of the cation plays an important role in the coordination polymer. Each Co center coordinates to two pyridyl nitrogen atoms of the two bipyridyl ligands and to two nitrate groups in a bidentate fashion. But the equatorially coordinating oxygen atoms are not planar with a maximum deviation of 0.9217 Å from the idealized plane defined by the Co and four oxygen atoms. The dihedral angle between the two nitrate groups is 87° and it is too small for the ligand to coordinates to Co ion from the front of the dihedral angle. In order to minimize steric hindrance between the bulky ligands and two nitrate groups, both the ligands coordinate to Co from the back of the nitrate groups forming a N(1)-Co(1)-N(1A) angle of 100.62°, such that the ligands coordinate to Co ion center in a *cis* configuration. The nitrate groups coordinate very unsymmetrically to Co in a bidentate fashion with Co-O distances of 2.065(3) and 2.264(3) Å; one Co-O distances are smaller to those of other known cobalt complexes containing bidentate nitrate groups (2.12–2.15 Å) [20–22]. The Co–N bond length of 2.065(3) Å is comparable to those of



Fig. 3. 1-D zig-zag infinite chain structure of 1 (H atoms have been omitted for clarity. Red: O; blue: N; green: Cd and white C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Packing diagram for 1.



Fig. 5. Molecular structure and atom numbering of 2.

related cobalt complexes containing pyridyl ligands. The bond angle between Co and two nitrogen atoms (N(1)–Co(1)-N(1A)) is 101°.

The cyclic units share further Co atoms forming an infinite 1D chain along a crystallographic axis in the *a* direction, as shown in Fig. 6. In the chain all nitrate groups are on the same side of the chain and the ligands are all on the other side, which is different from the zig-zag chain of complex 1. The adjacent chains are linked by the C– H…O to form plane. The bond length of C–H…O is 2.369 Å and the angle of C–H…O is 158.61°. The planes of the adjacent molecules are similarly separated by 3.654 Å, suggesting π – π stacking interactions (Fig. 7), as complex 1.

3.4. UV-vis spectra

The electronic absorption spectra of the free ligand, complex 1 and 2 ($c = 10^{-5} \text{ mol } \text{L}^{-1}$) were measured in DMF solutions. All the compounds (L, 1 and 2) exhibit essentially the same absorption profile: an intense and low-lying (near UV region) absorption band at 354 nm. Their electronic origins are proposed to be similar because of the comparable absorption coefficients. The large molar absorption coefficients ($\varepsilon = 2.1 \times 105 \text{ L mol}^{-1} \text{ cm}^{-1}$) are indicative of highly π -conjugated systems.



Fig. 7. Packing diagram for 2.



Fig. 6. 1-D infinite chain structure of 2 (H atoms have been omitted for clarity. Red: O; blue: Cd and white C). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 8. Fluorescent spectrum of complex 1 and 2 in the solid state at room temperature.

3.5. Photoluminescence

The luminescent properties of free ligand and its metal complexes were investigated in solid state at room temperature. The Cd and Co compounds exhibit broad emission bands with the maximum intensity at 524 and 545 nm, upon excitation at 350–450 nm and are red-shifted 48 and 73 nm compared to the emission wavelength of the free ligand, respectively. Generally, the intraligand and fluorescence emission wavelength is determined by the energy gap between π and π^* molecular orbitals of the free ligand, which is simply related to the extent of π conjugation in the system [23]. This large red shift reveals stronger interactions than that of the ligands between molecules and is the result of significant π - π^* stacking of the aromatic rings [24]. The luminescent properties of the free ligand and its metal complexes were investigated in solid state at room temperature (Fig. 8).

3.6. Thermal stability

To study the thermal stability of the free ligand and complex 1 and 2, thermal gravimetric analyses (TGA) were performed on the single crystal samples. There was no obvious weight loss until the temperature was increased to 320, 355 and 340 for L, 1 and 2, correspondingly, which showed fairly high thermal stabilities, especially for 1 and 2. It is obviously that the decomposition temperature of the polymers is higher than that of their free ligand. So it can be concluded that coordination of the ligand to the metal ion results in greater thermal stability.

Acknowledgements

This work was supported by a grant for the National Natural Science Foundation of China (50532030, 50325311,50335050), Doctoral Program Foundation of the Ministry of Education of China, Education Committee of Anhui Province (2006KJ032A, 2006KJ135B), Person with Ability Foundation of Anhui Province 2002Z021, The Team for Scientific Innovation Foundation of Anhui Province (2006KJ007TD), key Laboratory of Opto-Electronic Information Acquisition and Manipulation (Anhui University), Ministry of Education, person with Ability Foundation of Anhui University.

Appendix A. Supplementary data

Crystallographic data have been deposited with the CCDC (12 Union Road, Cambridge CB21EZ, UK, Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk; www: http://www.ccdc.cam.ac.uk) and are available on request quoting the deposition number CCDC227580 for 1; CCDC227583 for 2. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molstruc.2007.03.019.

References

- J. Kitagawa, R. Kitaura, S. Noro, Angew. Chem. Int. Ed. 43 (2004) 2334.
- [2] C. Janiak, Dalton Trans. (2003) 2781.
- [3] S.L. James, Chem. Soc. Rev. 32 (2003) 276.
- [4] S. Takamizawa, E. Nakata, H. Yokoyama, K. Mochizuki, W. Mori, Angew. Chem. Int. Ed. 42 (2003) 4331.
- [5] X.H. Bu, M.L. Tong, H.C. Chang, S. Kitagawa, S.R. Batten, Angew. Chem. Int. Ed. 43 (2004) 192.
- [6] M. Du, X.H. Bu, Y.M. Guo, J. Ribas, Chem. Eur. J. 10 (2004) 1345.
- [7] B. Sui, W. Zhao, G.H. Ma, T.A. Okamura, J. Fan, Y.Z. Li, S.H. Tang, W.Y. Sun, N. Ueyama, J. Mater. Chem. 14 (2004) 1631.
- [8] D.M. Skin, I.S. Lee, Y.K. Chang, M.S. Lah, Inorg. Chem. 42 (2003) 5459.
- [9] C.A. Johns, G.M.G. Hossian, K.M.A. Malik, S.Z. Haider, U.K.R. Romman, Polyhedron 20 (2001) 721.
- [10] A.J. Blake, N.R. Champness, A. Khlobystov, Chem. Commun. (1997) 2027.
- [11] A.M. Beatty, Coord. Chem. Rev. 246 (2003) 131.
- [12] H.W. Roesky, M. Andruh, Coord. Chem. Rev. 236 (2003) 91.
- [13] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798.
- [14] J.L. Seura, R. Gomez, N. Martin, D.M. Guldi, Org. Lett. 3 (2001) 2645.
- [15] M.S. Wong, Z.H. Li, M.F. Shek, M. Samoc, Chem. Mater. 14 (2002) 2999.
- [16] C.C. Kwok, M.S. Wong, Chem. Mater. 14 (2002) 3158.
- [17] J. Brunel, O. Mongin, A. Jutand, I. Ledoux, J. Zyss, Chem. Mater. 15 (2003) 4139.
- [18] M. Figita, O. Sasaki, K.Y. Watanabe, K. Ogura, K. Yamaguchi, New J. Chem. (1998) 189.
- [19] M. Fugita, Y.J. Kwon, M. Miyazawa, K. Ogura, J. Chem. Soc. Chem. Commun. (1994) 1977.
- [20] Y. Yamamoto, Y. Azuma, H. Mitoh, Synthesis (1986) 564.
- [21] K.N. Power, T.L. Hennigar, M.J. Zaworotko, New J. Chem. (1998) 177.
- [22] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, Angew. Chem. Int. Ed. Engl. 36 (1997) 1725.
- [23] M.W. Perkovic, Inorg. Chem. 39 (2000) 4962.
- [24] X.J. Zhang, J.Y. Wu, M.L. Zhang, Y.P. Tian, Trans. Metal Chem. 28 (2003) 707.