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A new one-dimensional Cd^{II} complex, $[Cd(\mu_2-L)_2]_n$ (HL=3-(2-pyridyl)pyrazole) with planar $[Cd(\mu_2-L)]_2$ unit: synthesis, crystal structure and emission property

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Abstract

A new one-dimension complex, $[Cd(\mu_2-L)_2]_n$ (1, HL=3-(2-pyridyl)pyrazole), has been hydrothermally synthesized and characterized by elemental analysis, IR, TGA, and single-crystal X-ray diffraction analysis. In 1, the L ligand takes tridentate chelating-bridging coordination mode via deprotonation of the pyrazolyl NH group and coordination of the pyrazolyl N atom to a second metal ion. In the solid state, complex 1 shows blue photoluminescent property at room temperature.

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Keywords: Cd^{II} complex; Crystal structure; Hydrothermal synthesis; 3-(2-Pyridyl)pyrazole; Luminescence

1. Introduction

Considerable attention has currently been paid to the study of coordination polymers owing to their fascinating structures and potential applications [1]. The combination of organic ligand 'spacers' and metal ion 'nodes' has been regarded as the most common synthetic approach to produce such coordination polymers [2]. In a spontaneous self-assembly process, the structural information stored in both the organic ligand and the metal ion is read out by the coordination through their coordination geometry [1c,3]. Thus, it is one of the key factors to choose the appropriate ligand and metal ion with favored coordination geometry for elaborating a specific architecture. 3-(2-Pyridyl)pyrazole (HL) firstly reported by Tisler and coworkers [4], is a multi-functional ligand having several coordination modes (Chart 1). Heretofore, the coordination chemistry of HL with some metal ions, Fe^{II} [5], Fe^{III} [6], Ni^{II} [5a,7], Cu^I [8], Cu^{II} [7,9], Zn^{II} [7], Ag^I [8], and Ti^I [8] has been studied by several groups. Recently, we have investigated the coordination chemistry of HL with Cu^{II} [10]. However, to the best of our knowledge, the Cd^{II} complex with this ligand has

not been reported. Herein, we report the hydrothermal synthesis and crystal structure of a new Cd^{II} complex, $[Cd(\mu_2-L)_2]_n$ (HL=3-(2-pyridyl)pyrazole). In addition, the emission property of this compound was also studied in the solid state at room temperature.

2. Experimental

2.1. Materials and general methods

All commercially available reagents for synthesis and analyses were of analytical grade and used as received without further purification. 3-(2-Pyridyl)pyrazole (HL) was synthesized according to the literature procedure [11]. Elemental analyses were performed on a Perkin–Elmer 240C analyzer. IR spectra were measured on a TENSOR 27 (Bruker) FT-IR spectrometer with KBr pellets in the range 4000–400 cm⁻¹. The X-ray powder diffraction (XRPD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Thermal analysis was carried out on a Rigaku standard TG-DTA analyzer from room temperature to 600 °C. Emission spectra were taken on a WGY-10 spectrofluorometer.

2.2. Synthesis of $[Cd(\mu_2-L)_2]_n$ (1)

A mixture of $Cd(NO_3)_2 \cdot 6H_2O$ (0.1 mmol) and HL (0.2 mmol) in H₂O (12 mL) was transferred and sealed in a

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Chart 1.

20 mL Teflon-lined stainless vessel, which was heated at 160 °C for 48 h and then cooled to room temperature at a rate of 5 °C h⁻¹. Colorless block crystals of **1** were obtained with the yield of 40%. Anal. Calcd for $C_{16}H_{12}CdN_6$: C, 47.96; H, 3.02; N 20.97. Found: C, 48.21; H, 3.15; N 20.78. IR (KBr pellet, cm⁻¹): 1597s, 1566m, 1519m, 1451m, 1426m, 1345m, 1275w, 1152w, 1118w, 1091w, 1062m, 1006w, 974m, 942m, 866m, 793w, 755s, 709m, 653m, 633m, 469w.

2.3. X-ray crystallography

Single-crystal X-ray diffraction was carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator at 293(2) K with Mo K α radiation (λ = 0.71073 Å) by ω scan mode. Unit cell dimensions were obtained with least-squares refinements and semi-empirical absorption corrections were applied using sADABS program [12]. The structure was solved by direct method [13]. The Cd^{II} ions were located from E-maps and the other non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods on F^2 by sHELXL – 97 program package

Table 1

Crystal data and structure refinement summary for complex 1

Empirical formula	$C_{16}H_{12}CdN_6$
Formula weight	400.72
Space group	<i>P</i> -1
a (Å)	8.026(2)
b (Å)	9.575(3)
c (Å)	11.020(3)
α (°)	75.832(5)
β (°)	85.124(5)
γ (°)	75.041(5)
Volume (Å ³)	793.1(4)
Ζ	2
$D_{\text{calcd}} (\text{g/cm}^3)$	1.678
Т (К)	293(2)
λ (Mo K α) (Å)	0.71073
$\mu (\mathrm{mm}^{-1})$	1.384
F (000)	396
Range of h, k, l	-5/9, -11/11, -13/12
Reflections collected/unique	4259/2896
Max. and min. transmission	0.9340 and 0.7598
Data/restraints/parameters	2896/0/208
Goodness-of-fit on F^2	1.017
$R^{\rm a}$ and $wR^{\rm b}$	0.0649 and 0.0987
Largest diff. peak and hole $(e/Å^3)$	0.592 and -0.532

^a $R = \Sigma(||F_0| - |F_c||)/\Sigma|F_0.$

^b $wR = [\Sigma w(|F_0|^2 - |F_c|^2)^2 / \Sigma w(F_0^2)]^{1/2}.$

[13]. Hydrogen atoms were included in calculated positions and refined with fixed thermal parameters riding on the parent atoms. Crystallographic data and experimental details for structural analysis are summarized in Table 1, and selected bond lengths and angles are presented in Table 2. The crystal data file in CIF format was deposited in CCDC (no. 288877). This data can be obtained from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk.

3. Results and discussion

3.1. Synthesis, spectral characterization and thermal analysis

Complex 1 was synthesized by the hydrothermal method at 160 °C without adding any base for adjusting the pH value. The IR spectrum of 1 shows absorption bands resulting from the skeletal vibrations of the aromatic rings in the 1400–1600 cm⁻¹ range, and there is no absorption band beyond 3000 cm^{-1} , indicating deprotonation of the pyrazole NH group, which is consistent with the X-ray analysis.

The thermal behavior of complex 1 was studied from room temperature to 600 °C. The TGA curve indicates that 1 experienced one step of weight-loss. It began to decompose at 417 °C and ended at about 476 °C (observed weight-loss 67%, theoretical weight-loss 67.96%). The final residue should be CdO.

3.2. Description of the crystal structure

Table 2

The single-crystal X-ray analysis shows that complex **1** has a one-dimensional polymeric structure with the neutral $[Cd(\mu_2-L)_2]$ as repeating unit. As shown in Fig. 1a, the local

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Selected bond	lengths (Å) and angles $(^{\circ})$ for complex 1

Cd(1)–N(3)	2.265(7)	Cd(1)–N(6)	2.272(6)
Cd(1)-N(5A)	2.279(6)	Cd(1)–N(2)	2.296(6)
Cd(1)-N(4)	2.434(7)	Cd(1)–N(1)	2.496(8)
N(3)-Cd(1)-N(6)	97.3(2)	N(3)-Cd(1)-N(5A)	95.2(2)
N(6)-Cd(1)-N(5A)	99.5(2)	N(3)-Cd(1)-N(2)	98.3(2)
N(6)-Cd(1)-N(2)	98.1(2)	N(5A)-Cd(1)-N(2)	156.2(2)
N(3)-Cd(1)-N(4)	90.8(2)	N(6)-Cd(1)-N(4)	167.5(3)
N(5A)-Cd(1)-N(4)	70.2(3)	N(2)-Cd(1)-N(4)	90.1(3)
N(3)-Cd(1)-N(1)	165.1(2)	N(6)-Cd(1)-N(1)	92.8(2)
N(5A)-Cd(1)-N(1)	93.8(3)	N(2)-Cd(1)-N(1)	69.4(3)
N(4)-Cd(1)-N(1)	81.2(2)		

Symmetry code: A: -x+1, -y+1, -z+1.

coordination environment around Cd^{II} ion in **1** is formed by four chelating-bridging ligands L, which plays two types of roles, chelating one Cd^{II} center and simultaneously bridging the other one, showing a tridentate chelating-bridging mode. The Cd^{II} ion has a slight distorted octahedral coordination geometry comprised of six nitrogen atoms (four pyrazolyl N and two pyridyl N) of four distinct L ligands (Cd–N lengths 2.265(7)–2.496(8) Å), and the bond angles around the Cd^{II} center range from 69.4(3) to 167.5(3)°. The important bond distances and angles are listed in Table 2. It is noteworthy that the Cd–N_{pyridyl} distances (2.434(7) and 2.496(8) Å) are longer than those of Cd–N_{pyrazolyl} (2.265(7)–2.296(6) Å).

In the crystal structure of **1**, two L ligands bridge two Cd^{II} ions by deprotonated pyrazolyl NH groups to form two kinds of approximately planar $[Cd(\mu_2-L)]_2$ binuclear structure units (Fig. 1b) containing six-membered ring, $(Cd-N-N-)_2$, in which, the Cd···Cd distance is 4.291 and 4.336 Å, respectively, and the two $[Cd(\mu-L)]_2$ planes are almost vertical with each other (the dihedral angle is 92.9°) (Fig. 1c). As shown in Fig. 2, along the one-dimension chain, the two kinds of planar binuclear units present alternately and the adjacent binuclear units share one metal center, with the Cd–Cd–Cd angle being 136.99°.

In 1, HL acts as a tridentate chelating-bridging ligand via deprotonation of the pyrazole NH group (Chart 1b). The coordination mode of the ligand in 1 is very similar to Cu^{II} complexes [10]. And the assembly of these structures is directed by the stereochemical preference of the M^{II} (M=Cu^{II}, Cd^{II}) ions: to fulfill this requirement necessitates deprotonation of the pyrazolyl groups to form planar [M(μ_2 -L)]₂ (M=Cu^{II}, Cd^{II}, HL=3-(2-pyridyl)pyrazole) binuclear unit. Apparently, this coordination mode is different from that of the same ligand with other first-row transition metal ions Zn^{II} [7] and Ni^{II} [5a,7] in which HL was just considered as a simple bidentate chelating ligand.

3.3. XRPD result

In order to confirm the phase purity of the bulk materials, X-ray powder diffraction (XRPD) experiment has been carried out for complex **1**. The XRPD experimental and computersimulated patterns of **1** are shown in Fig. 3. Although there are some slight differences between the experimental pattern and the calculated pattern based on the result from single-crystal X-ray diffraction, it still can be well considered that the bulk synthesized materials and the as-grown crystals are homogeneous for complex **1**.

3.4. Photoluminescence properties

The excitation and emission spectra of 1 in the solid state at room temperature are shown in Fig. 4. It can be observed that complex 1 exhibits blue photoluminescence with an emission maximum at ca. 367 nm upon excitation at 303 nm. This emission is neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal transfer (LMCT) in nature since the Cd^{II} ion is difficult to oxidize or to reduce due to its d¹⁰ configuration



Fig. 1. View of (a) the coordination environment of Cd^{II} in **1** with all H atoms omitted for clarity (symmetry code for A: 1-x, 1-y, 1-z); (b) the planar [Cd(μ_2 -L)]₂ binuclear unit (symmetry code for A: 1-x, 1-y, 1-z); and (c) the two kinds of planar binuclear units, showing the perpendicularity of them which are sharing one metal center (symmetry codes for A: 1-x, 1-y, 1-z; B: 2-x, 1-y, 1-z).



Fig. 2. Perspective view of the 1D chain of 1 propagated along the crystallographic a-axis.

which can probably be assigned to the intraligand $(\pi - \pi^*)$ fluorescent emission [14]. Many aromatic ligands, which are not strongly emissive on their own, show much stronger luminescence when coordinated to Cd^{II} or Zn^{II} [15]. These enhancements are perhaps a result of coordination of those ligands to Cd^{II} (or Zn^{II}), which increases the ligands'



Fig. 4. Emission and excitation spectra of 1 at room temperature.

conformational rigidity, thereby reducing the non-radiative decay of the intraligand $(\pi - \pi^*)$ excited state [15,16].

In summary, a new one-dimension Cd^{II} complex has been hydrothermally synthesized and characterized, and its luminescent properties have also been investigated. It is notable to point out that in order to fit the coordination geometry of the metal ion, the ligand in **1** adopts the deprotonation mode of the pyrazoly NH group and the coordination of the pyrazolyl N atom to a second metal ion.

Acknowledgements

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References

- For examples B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629;
 M. Eddaoudi, D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe,
 O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319; Z. He, Z.M. Wang,
 C.H. Yan, Cryst. Eng. Commun. 7 (2005) 143.
- [2] For examples W.P. Su, M.C. Hong, J.B. Weng, R. Cao, S.F. Lu, Angew. Chem. Int. Ed. 39 (2000) 2911; W. Chen, H.M. Yuan, J.Y. Wang, Z.Y. Liu, J.J. Xu, M. Yang, J.S. Chen, J. Am. Chem. Soc. 125 (2003) 9266; M.L. Tong, X.M. Chen, S.R. Batten, J. Am. Chem. Soc. 125 (2003) 16170; W.S. Liu, T.Q. Jiao, Y.Z. Li, Q.Z. Liu, M.Y. Tan, H. Wang, L.F. Wang, J. Am. Chem. Soc. 126 (2004) 2280; C.M. Liu, S. Gao, D.Q. Zhang, Y.H. Huang, R.G. Xiong, Z.L. Liu, F.C. Jiang, D.B. Zhu, Angew. Chem. Int. Ed. 43 (2004) 990; X.H. Bu, M.L. Tong, H.C. Chang, S. Kitagawa, S.R. Batten, Angew. Chem. Int. Ed. 43 (2004) 192.
- [3] J.M. Lehn, Supramolecular Chemistry-Concepts and Perspectives, VCH, Weinheim, 1995.
- [4] M. Tisler, B. Stanovnik, B. Versek, Vestn. Slov. Kem. Drus. 27 (1980) 65.
- [5] K.H. Sugiyarto, H.A. Goodwin, Aust. J. Chem. 41 (1988) 1645;
 L.S. Harimanow, K.H. Sugiyarto, M.L. Craig, H.A. Goodwin, Aust. J. Chem. 52 (1999) 109; B.A. Leita, B. Moubaraki, K.S. Murray, J.P. Smith, J.D. Cashion, Chem. Commun. (2004) 156.
- [6] P.L. Jones, J.C. Jeffery, J.A. McCleverty, M.D. Ward, Polyhedron 16 (1997) 1567.
- [7] K.L.V. Mann, E. Psillakis, J.C. Jeffery, L.H. Rees, N.M. Harden, J.A. McCleverty, M.D. Ward, D. Gatteschi, F. Totti, F.E. Mabbs, E.J.L. McInnes, P.C. Riedi, G.M. Smith, J. Chem. Soc., Dalton Trans. (1999) 339.
- [8] K. Singh, J.R. Long, P. Stavropoulos, J. Am. Chem. Soc. 119 (1997) 2942.
- [9] J.C. Jeffery, P.L. Jones, K.L.V. Mann, E. Psillakis, J.A. McCleverty, M.D. Ward, Chem. Commun. (1997) 175.

- [10] T.L. Hu, J.R. Li, C.S. Liu, X.S. Shi, J.N. Zhou, X.H. Bu, J. Ribas, Inorg. Chem. 45 (2006) 162, and references therein.
- [11] H. Brunner, T. Scheck, Chem. Ber. 125 (1992) 701; A.J. Amoroso, M.W. Cargill Thompson, J.C. Jeffery, P.L. Jones, J.A. McCleverty, M.D. Ward, Chem. Commun. (1994) 2751; F. Wang, A.W. Schwabacher, Tetrahedron Lett. 40 (1999) 4779.
- [12] G.M. Sheldrick, SADABS Siemens Area Detector Absorption Corrected Software, University of Göttingen, Germany, 1996.
- [13] G.M. Sheldrick, SHELXTL NT Version 5.1. Program for Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [14] L.L. Wen, D.B. Dang, C.Y. Duan, Y.Z. Li, Z.F. Tian, Q.J. Meng, Inorg. Chem. 44 (2005) 7161.
- [15] J. Zhang, Y.R. Xie, Q. Ye, R.G. Xiong, Z. Xue, X.Z. You, Eur. J. Inorg. Chem. (2003) 2572 and references therein..
- [16] J. Lu, K. Zhao, Q.R. Fang, J.Q. Xu, J.H. Yu, X. Zhang, H.Y. Bie, T.G. Wang, Cryst. Growth Des. 5 (2005) 1091.