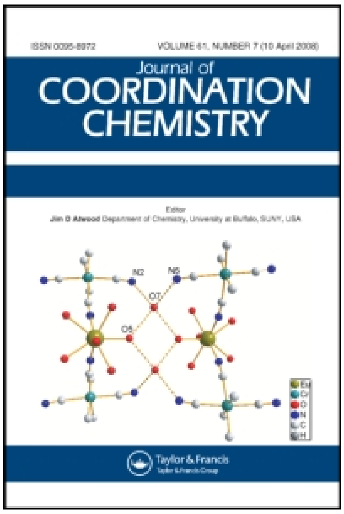

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and structural characterization of a novel coordination polymer [Cd$_2$(SCN)$_2$(C$_8$H$_6$NO$_2$)$_2$(H$_2$O)$_4$]*_n*

Yan-Ji Wang[a]; Qiu-Xiang Zhou[a]; Lin Yue[a]; Xin-Qiang Zhao[a]
[a] School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, P.R. China

To cite this Article Wang, Yan-Ji , Zhou, Qiu-Xiang , Yue, Lin and Zhao, Xin-Qiang(2004) 'Synthesis and structural characterization of a novel coordination polymer [Cd$_2$(SCN)$_2$(C$_8$H$_6$NO$_2$)$_2$(H$_2$O)$_4$]*_n*', Journal of Coordination Chemistry, 57: 9, 741 — 746

To link to this Article: DOI: 10.1080/00958970410001721006

URL: http://dx.doi.org/10.1080/00958970410001721006

J. Coord. Chem., Vol. 57, No. 9, 15 June 2004, pp. 741–746

Taylor & Francis
Taylor & Francis Group

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF A NOVEL COORDINATION POLYMER $[Cd_2(SCN)_2(C_8H_6NO_2)_2(H_2O)_4]_n$

YAN-JI WANG*, QIU-XIANG ZHOU, LIN YUE
and XIN-QIANG ZHAO

School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, P.R. China

(Received 11 November 2003; In final form 24 April 2004)

A new three-dimensional organic/inorganic coordination polymer was synthesized by the hydrothermal reaction of $Cd(CH_3COO)_2 \cdot 2H_2O$, KSCN and 3-(3-pyridyl)acrylic acid. The product $[Cd_2(SCN)_2(C_8H_6NO_2)_2(H_2O)_4]_n$ has an infinite three-dimensional structure with a diamondoid network. It crystallizes in the triclinic system, space group $P\bar{1}$ with $a = 6.961(2)$, $b = 10.308(3)$, $c = 16.944(6)$ Å, $\alpha = 91.567(6)$, $\beta = 90.365(7)$, $\gamma = 98.385(6)°$. In this compound, the Cd(II) centers lie in an octahedral environment. The crystal structure of this compound was determined by single-crystal X-ray diffraction methods and it was characterized by elemental analysis (EA), infrared spectra (IR) and thermogravimetric and differential thermal analysis (TG-DTA). The results demonstrate the feasibility of constructing a crystalline metal-organic coordination polymer and also provide a starting point for the design of more robust and potentially functional materials.

Keywords: Coordination polymer; Hydrothermal reaction; Crystal structure

INTRODUCTION

The construction of metal-organic coordination polymers has developed rapidly in recent years, because of their interesting molecular topologies and potential properties as functional materials [1–8]. Although many coordination polymers have been synthesized by self assembly, syntheses of porous coordination networks of such complicated supramolecular compounds are still major challenges.

Rigid ligands and flexible ligands have been used to synthesize porous metal-organic frameworks [9,10]. The majority of rigid linking ligands are based on either neutral donor ligands or strictly anionic groups. As neutral donor ligands [11–13], 4,4′-bpy, pyrazine and *trans*-1,2-bis(4-pyridyl)ethane, which contain two nitrogen are chosen in order to generate 1-D, 2-D and 3-D coordination polymers. On the other hand, rigid polycarboxylates [14–15], such as 1,3,5-benzenetricarboxylate, and 1,4-benzenedicarboxylate, have been used as anionic linkers which can stabilize many structures with

---

*Corresponding author. Fax: +86-22-26564287. E-mail: yjwang@hebut.edu.cn

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001721006

open frameworks. Our research in this area focuses on coordination polymers with multifunctional ligands. In this work, we use 3-(3-pyridyl)acrylic acid in which neutral and anionic donor groups are included. We hope that both neutral and anionic donor groups in such bridging ligands can coordinate to metal centers to produce a polymeric structure. Although there have been some reports on 3-(3-pyridyl)acrylic acid, using SCN^- as a small connecting ligand has not been reported. We have succeeded in synthesizing a new coordination polymer $[Cd_2(SCN)_2(C_8H_6NO_2)_2(H_2O)_4]_n$ which has a 3-D structure bridging two ligands. Herein, the title polymer is characterized by EA, IR, single-crystal X-ray diffraction analysis, and TG-DTA.

EXPERIMENTAL

Materials and Synthesis

The ligand was obtained commercially from ACROS and used as received. The complex was prepared as follows: 3-(3-pyridyl)acrylic acid (0.1504 g,1 mmol) was thoroughly mixed in distilled water (4 cm^3) until completely dissolved. Then KSCN (0.1979 g, 2 mmol) and 3 cm^3 aqueous $Cd(CH_3COO)_2 \cdot 2H_2O$ (0.2669 g, 1 mmol) solution was added. After the mixture was blended completely, it was sealed in a Teflon-lined autoclave and heated at 120°C under autogenous pressure. The solution was kept at this temperature for 48 h, then cooled to 40°C White crystals were obtained. Anal. Calcd. for $C_{18}H_{20}N_4O_8S_2Cd_2$(%): C, 30.47; H, 2.82; N, 7.90. Found: C, 30.41; H, 2.76; N, 7.98. IR (KBr, cm^{-1}): 3422(s), 1649(m), 1560(s), 1488(w), 1428(m), 1399(m), 1381(m), 1264(w), 979(w), 809(w), 689(w).

Physical Measurements

EA for C, H and N was performed on a Perkin-Elmer 240 instrument. IR analysis was performed for the compound in a KBr pellet with a Bruker Vector 22 spectrophotometer in the 4000–400 cm^{-1} region. TG-TGA was performed under air flow at a heating rate of 10°C min^{-1} in the 20–700°C region.

X-ray Crystallography

A single crystal with dimensions (0.08 × 0.06 × 0.04 mm) was used for data collection on a Bruker Smart 1000 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.071073$ nm) at 298 K. Least-squares refinement of their setting angles in the 2θ range 1.20–25.0° gave rise to the unit cell parameters. The structure was solved by direct methods using the SHELXTL-97 package. All the non-hydrogen atoms were located and refined anisotropically. Hydrogen atoms were located from the difference Fourier maps and refined isotropically. Molecular drawings were produced by the SHELXTL-XP program.

Crystal Data

The complex crystallizes in the triclinic system, space group $P\bar{1}$. $C_{18}H_{20}N_4O_8S_2Cd_2$, $M = 709.30$, $a = 6.961(2)$, $b = 10.308(3)$, $c = 16.944(6)$ Å, $\alpha = 91.567(6)$, $\beta = 90.365(7)$,

$\gamma = 98.385(6)^\circ$, $F(000) = 696$, $Z = 2$, $V = 1202.4(7)\,\text{Å}^3$, $R1[I > \neq \sigma(I)] = 0.0719$, $wR2[I > 2\sigma(I)] = 0.0913$.

RESULTS AND DISCUSSION

Crystal Structures

The polymer was obtained as white columnar crystals by a hydrothermal reaction between $Cd(CH_3COO)_2{\cdot}2H_2O$, KSCN and 3-(3-pyridyl)acrylic acid in water at 120°C. In the crystal structure of $[Cd_2(SCN)_2(C_8H_6NO_2)_2(H_2O)_4]_n$, each Cd(II) atom has a distorted octahedral coordination geometry. Each Cd(II) is in a different coordination mode, linked by SCN^- and 3-(3-pyridyl)acrylic acid ligands. Selected bond lengths and angles are given in Table I.

The unit, $[Cd_2(SCN)_2(C_8H_6NO_2)_2(H_2O)_4]_n$, was synthesized through self-assembly of metal with a preference for a particular coordination geometry. A crystallographic analysis of $[Cd_2(SCN)_2(C_8H_6NO_2)_2(H_2O)_4]_n$ exhibited a 3-D structure constructed from the $[Cd_2(SCN)_2(C_8H_6NO_2)_2(H_2O)_4]$ basic unit, as shown in Figs 1 and 2. Both types of Cd^{II} ions are in slightly distorted octahedral coordination environments. Cd(1) is coordinated by three oxygen atoms and one nitrogen from three 3-(3-pyridyl)acrylic acid molecules, one oxygen from water and one sulfur from SCN^-. The Cd(1)–O bonds range from 2.234(10) to 2.645(10) Å, while Cd(1)–N and Cd(1)–S bond lengths are 2.296(11) and 2.641(5) Å, respectively. Cd(1) and Cd(2) within a building block are connected by one 3-(3-pyridyl)acrylic acid ligand which acts as a longer spacing ligand than the isonicotinate ligand, forming more porous materials. The Cd(2) atom is coordinated by three nitrogen atoms from one 3-(3-pyridyl)acrylic acid and two SCN^-, one sulphur from SCN^- and two oxygens from water. The Cd(2)–O(6) and Cd(2)–O(7) bonds are 2.361(9) and 2.341(10) Å, respectively. The Cd(2)–N bonds range from 2.264(14) to 2.361(10) Å, while the Cd(2)–S bond length is 2.703(5) Å. These bond lengths and angles are in the normal range. The building block units are connected by SCN^- so that 2-D diamondoid networks are formed.

TABLE I Selected bond lengths (Å) and angles (°) for $[Cd_2(SCN)_2(C_8H_6NO_2)_2(H_2O)_4]$

Cd(1)–O(3)	2.234(10)	Cd(1)–N(1)#1	2.296(11)	Cd(1)–O(1)	2.325(10)
Cd(1)–O(5)	2.393(10)	Cd(1)–S(1)	2.641(5)	Cd(1)–O(2)	2.645(10)
Cd(2)–N(3)#2	2.264(14)	Cd(2)–N(4)#3	2.308(15)	Cd(2)–O(7)	2.341(10)
Cd(2)–N(2)	2.361(10)	Cd(2)–O(6)	2.361(9)	Cd(2)–S(2)	2.703(5)
O(3)–Cd(1)–N(1)#1	132.3(4)	O(3)–Cd(1)–O(1)	134.2(4)	N(1)#1–Cd(1)–O(1)	87.9(4)
O(3)–Cd(1)–O(5)	75.3(4)	N(1)#1–Cd(1)–O(5)	96.5(4)	O(1)–Cd(1)–O(5)	79.8(4)
O(3)–Cd(1)–S(1)	96.0(3)	N(1)#1–Cd(1)–S(1)	98.1(3)	O(1)–Cd(1)–S(1)	98.8(3)
O(5)–Cd(1)–S(1)	165.2(3)	O(3)–Cd(1)–O(2)	89.3(4)	N(1)#1–Cd(1)–O(2)	138.3(4)
O(1)–Cd(1)–O(2)	53.0(3)	O(5)–Cd(1)–O(2)	90.6(3)	S(1)–Cd(1)–O(2)	77.2(2)
N(3)#2–Cd(2)–N(4)#3	93.0(5)	N(3)#2–Cd(2)–O(7)	88.1(5)	N(4)#3–Cd(2)–O(7)	175.1(4)
N(3)#2–Cd(2)–N(2)	174.9(5)	N(4)#3–Cd(2)–N(2)	91.2(5)	O(7)–Cd(2)–N(2)	87.4(4)
N(3)#2–Cd(2)–O(6)	87.2(4)	N(4)#3–Cd(2)–O(6)	87.7(4)	O(7)–Cd(2)–O(6)	87.6(4)
N(2)–Cd(2)–O(6)	90.0(4)	N(3)#2–Cd(2)–S(2)	92.5(4)	N(4)#3–Cd(2)–S(2)	95.5(3)
O(7)–Cd(2)–S(2)	89.2(3)	N(2)–Cd(2)–S(2)	90.0(3)	O(6)–Cd(2)–S(2)	176.8(3)

Symmetry transformations used to generate equivalent atoms: #1 $x, y-1, z$; #2 $-x+1, -y+1, -z+1$; #3 $-x+2, -y+1, -z+1$; #4 $x, y+1, z$.

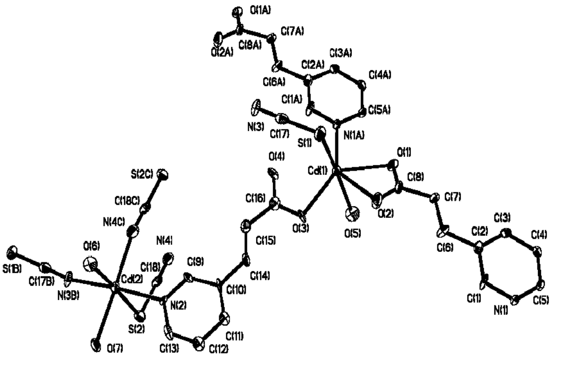

FIGURE 1 Coordination structure of the title polymer around the Cd centers.

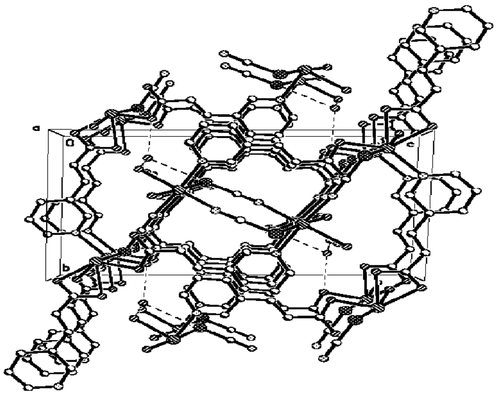

FIGURE 2 Packing diagram of the title polymer, viewed down the *a*-axis.

In addition, separation of the interlaced pyridyl rings along the *a*-axis is 3.805 Å, indicating π–π stacking interactions. The coordination water molecules, the carboxylate oxygen atoms and SCN^- interact with the crystallization water to form a hydrogen-bonding network, as shown in Table II. These diamondoid networks are connected through hydrogen bonds, so a 3-D structure is formed. The hydrogen-bonding and π–π stacking interactions further stabilize this 3-D network.

Infrared spectra show the characteristic bands of water molecules, the hydroxyl group in the 3000–3600 cm^{-1} range; the numerous bands located around 1500 cm^{-1} are attributed to the COO^- bonds of 3-(3-pyridyl)acrylic acid; and bonds of 1649 cm^{-1}, 1428 cm^{-1} and 1381 cm^{-1} represent pyridine groups. An IR spectrum is shown in Fig. 3.

A TG-DTA study indicated that water molecules are removed through two processes. The polymer started to lose crystallization water at around 82°C. At *ca.* 170°C, the coordination water began to be lost. Complete removal of all water content was achieved at around 270°C. The 5.3% weight loss corresponds to the removal of four equivalents of water per unit formula. Upon further heating, the dehydrated residue started to decompose at 350°C. Complete decomposition of the polymer is finished at *ca.* 550°C, suggesting that the ligands are strongly coordinated, consistent with the

TABLE II Hydrogen bond lengths (Å) and angles (°) for $[Cd_2(SCN)_2(C_8H_6NO_2)_2(H_2O)_4]$

D–H···A	*d(D–H)*	*d(H···A)*	*d(D···A)*	∠(DHA)
O(5)–H(5A)···O(1)#5	0.85	1.89	2.736(13)	179.4
O(5)–H(5B)···S(1)#6	0.85	2.68	3.532(11)	179.4
O(6)–H(6A)···O(8)	0.84	2.38	3.212(13)	176.8
O(6)–H(6B)···O(4)#2	0.84	1.85	2.693(14)	177.3
O(7)–H(7A)···O(8)#6	0.85	1.92	2.744(14)	163.8
O(7)–H(7B)···O(2)#7	0.85	2.19	2.870(13)	136.9
O(8)–H(8A)···O(3)#7	0.86	1.93	2.789(15)	179.3
O(8)–H(8B)···S(2)#8	0.86	2.38	3.240(12)	179.4

Symmetry transformations used to generate equivalent atoms: #1 $x, y-1, z$; #2 $-x+1, -y+1, -z+1$; #3 $-x+2, -y+1, -z+1$; #4 $x, y+1, z$; #5 $-x+1, -y+2, -z$; #6 $x+1, y, z$; #7 $-x+1, -y+2, -z+1$; #8 $x-1, y, z$.

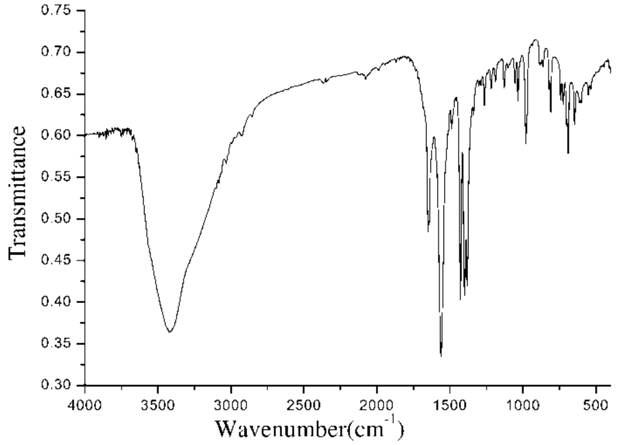

FIGURE 3 IR spectra of the title polymer.

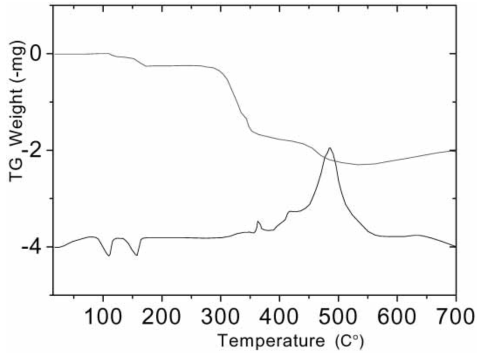

FIGURE 4 TG-DTA curves of the title polymer.

structure, and accounts for the coordination polymer being rather stable. After 520°C, the weight of the residue began to increase because of the production of cadmium oxide in the oxygen, as indicated by its X-ray powder diffraction pattern. TG-DTA curves are shown in Fig. 4.

In summary, we have structurally characterized $[Cd_2(SCN)_2(C_8H_6NO_2)_2(H_2O)_4]_n$, which was prepared from $Cd(CH_3COO)_2 \cdot 2H_2O$, KSCN and 3-(3-pyridyl)acrylic acid by a hydrothermal reaction. This coordination polymer is stable at normal temperatures. We will continue to study its properties in catalysis and magnetism.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (No: 20176008).

Supplementary Data

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Center, CCDC No. 221823 for the title coordination polymer. Copies of this information may be obtained free of charge via the internet at www.ccdc.cam.ac.uk or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] M. Fujita, S.Y. Yu, T. Kusukawa, H. Funaki, K. Ogura and K. Yamaguchi, *Angew. Chem. Int. Ed. Engl.* **37**, 2082 (1998).
[2] Y.H. Liu, C.S. Lin, S.Y. Chen, H.L. Tsai, C.H. Ueng and K.L. Lu, *J. Solid State Chem.* **157**, 166 (2000).
[3] P. Ayyappan, O.R. Evans and W. Lin, *Inorg. Chem.* **40**, 4627 (2001).
[4] Y.C. Liang, M.C. Hong, R. Cao, W.P. Su, Y.J. Zhao, J.B. Weng and R. G. Xiong, *Bull. Chem. Soc. Jpn.* **75**, 1521 (2002).
[5] W.Z. Chen, F.H. Liu and X.Z. You, *Bull. Chem. Soc. Jpn.* **75**, 1559 (2002).
[6] L.C. Tabares, J.A.R. Navarro and J.M. Salas, *J. Am. Chem. Soc.* **123**, 383 (2001).
[7] J. Zhu, X.H. Bu, P.Y. Feng and G.D. Stucky, *J. Am. Chem. Soc.* **122**, 11563 (2000).
[8] O.R. Evans and W. Lin, *Inorg.Chem.* **39**, 2189 (2000).
[9] J.Y. Baeg and S.W. Lee, *Inorg. Chem. Comm.* **6**, 313 (2003).
[10] J.H. Liao, S.H. Cheng and C.T. Su, *Inorg. Chem. Commun.* **5**, 761 (2002).
[11] S.-I. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka and M. Yamashita, *J. Am. Chem. Soc.* **124**, 2568 (2002).
[12] S.-I. Noro, S. Kitagawa, M. Kondo and K. Seki, *Angew. Chem. Int. Ed.* **39**, 2082 (2000).
[13] T.L. Hennigar, D.C. Macquarrie, P. Losier, R.D. Rogers and M.J. Zaworotko, *Angew. Chem. Int. Ed. Engl.* **36**, 972 (1997).
[14] K. Seki and W. Mori, *J. Phys. Chem. B* **106**, 1380 (2002).
[15] J.C. Dai, X.T. Wu, Z.Y. Fu, C.P. Cui, S.M. Hu, *et al.*, *Inorg. Chem.* **41**, 1391 (2002).