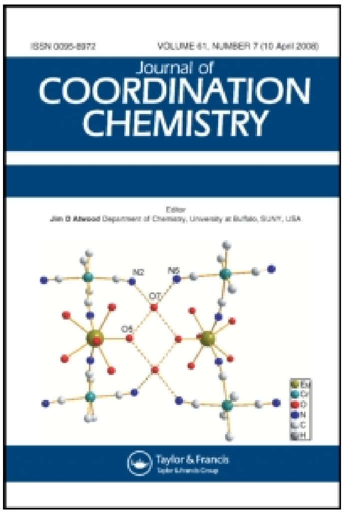


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, crystal structure and luminescence of a two-dimensional interpenetrating supermolecular complex {[Cd(phen)$_2$(sube)] · 2H$_2$O}_n

Yaguang Sun[a]; Xiaofu Gu[a]; Enjun Gao[a]; Dezhou Wei[b]; Xiaomei Yan[a]; F. Verpoort[c]
[a] Laboratory of Coordination Chemistry, Shenyang Institute of Chemical Technology, Shenyang 110142, China [b] School of Resource & Civil Engineering, Northeastern University, Shenyang 110004, China [c] Department of Inorganic and Physical Chemistry, Ghent University, Ghent 9000, Belgium

First published on: 19 September 2007

To cite this Article Sun, Yaguang , Gu, Xiaofu , Gao, Enjun , Wei, Dezhou , Yan, Xiaomei and Verpoort, F.(2008) 'Synthesis, crystal structure and luminescence of a two-dimensional interpenetrating supermolecular complex {[Cd(phen)$_2$(sube)] · 2H$_2$O}_n', Journal of Coordination Chemistry, 61: 8, 1165 — 1171, First published on: 19 September 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701572642

URL: http://dx.doi.org/10.1080/00958970701572642

Journal of Coordination Chemistry
Vol. 61, No. 8, 20 April 2008, 1165–1171

Taylor & Francis
Taylor & Francis Group

Synthesis, crystal structure and luminescence of a two-dimensional interpenetrating supermolecular complex $\{[Cd(phen)_2(sube)] \cdot 2H_2O\}_n$

YAGUANG SUN†, XIAOFU GU†, ENJUN GAO*†, DEZHOU WEI‡,
XIAOMEI YAN† and F. VERPOORT§

†Laboratory of Coordination Chemistry, Shenyang Institute
of Chemical Technology, Shenyang 110142, China
‡School of Resource & Civil Engineering, Northeastern University,
Shenyang 110004, China
§Department of Inorganic and Physical Chemistry,
Ghent University, Ghent 9000, Belgium

(*Received 4 February 2007; in final form 7 May 2007*)

A coordination polymer $\{[Cd(phen)_2(sube)] \cdot 2H_2O\}_n$ (**1**) (phen = 1,10-phenanthroline; H_2sube = suberic acid) has been synthesized by reaction of phen and suberic acid with cadmium(II). Elemental analysis, thermal analyses, IR spectra and X-ray crystal structure analysis were carried out to determine the composition and crystal structure of **1**. The Cd(II) is six-coordinate in a distorted octahedral configuration. A 2-D interpenetrating framework supramolecular structure was formed by π–π stacking interaction between phen of neighboring chains. Moreover, **1** displayed luminescent properties in the blue range at room temperature.

Keywords: Cadmium(II); Supramolecular; Suberic acid; Crystal structure; Interpenetrating

1. Introduction

Interest has focused on the rational design and synthesis of coordination polymers because they have unique structural motifs and tunable physical properties [1,2]. Rigid multicarboxylate ligands with aryl and *N*-heterocyclic rings such as 1,4-benzenedicarboxylate [3], 1,3,5-benzenetricarboxylate [4], pyridine-2,6-dicarboxylate [5], and pyridine-2,5-dicarboxylate [6] have been widely used because they have good donor atoms. Some dicarboxylate ligands containing aliphatic chains are also good candidates for construction of metal-organic frameworks. For example, adipate constructs macrocyclic polymers with transition or rare earth metal ions [7], by use of fumarate ligands, the interpenetrated diamondoid net of Ni(II) and large cavity framework complexes were observed [8]. In contrast, suberic acid, as a bicarboxylate acid is rarely used. However, its long and flexible chain provides an excellent strategy to construct coordination polymers with specific architectures. Herein, using suberic acid

---

*Corresponding author. Email: ejgao@yahoo.com.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2008 Taylor & Francis
DOI: 10.1080/00958970701572642

(H_2sube) as bridging ligands and 1,10-phenanthroline (phen) as terminal ligands, we successfully synthesized $\{[Cd(phen)_2(sube)] \cdot 2H_2O\}_n$ (**1**). X-ray structural analysis shows that the complex forms a 2-D interpenetrating framework supramolecular structure upon π–π stacking interaction between phens of adjacent chains. **1** also has blue luminescence at room temperature.

2. Experimental

2.1. *Reagent and physical measurements*

All chemicals were reagent grade obtained from commercial sources and used without further purification. C, H, N analyses were carried out with a Finnigan EA 1112 elemental analyzer. IR spectra were performed on a Nicolet 470 spectrometer with KBr pellets in the $4000 \sim 400\,cm^{-1}$ region. Thermal analyses was performed on a NETZSCH TG 209 instrument in flowing N_2 with a heating rate of $10^{\circ}C\,min^{-1}$. Excitation and emission spectra were obtained on a Perkin-Elmer LS55 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source.

2.2. *Synthesis of* $\{[Cd(phen)_2(sube)] \cdot 2H_2O\}_n$

0.5 mmol suberic acid was dissolved in 50 mL water. The resultant solution was mixed with 40 mL ethanol containing 1 mmol phen. Under stirring, 20 mL water containing 0.5 mmol $Cd(NO_3)_2$ was added slowly. During this time, the pH of the solution decreased gradually and $0.2\,mol\,L^{-1}$ KOH was used to adjust the pH to 8, and the solution was condensed with rotatory evaporator. About 40 mL condensed colorless transparent liquid was kept at room temperature. Colorless transparent crystals were obtained 10 d later. IR 3419(s), 2931(m), 1628(s), 1570(s), 1514(s), 1413(s), 1384(s), 1364(s), 1186(s), 855(s), 727(s) cm^{-1}. Anal. Calcd for $C_{32}H_{32}N_4O_6Cd$ (%): C, 56.43; H, 4.75; N, 8.23. Found (%): C, 56.33; H, 4.66; N, 8.15.

2.3. *X-ray structure determination*

A colorless single crystal with dimensions of 0.20 mm × 0.18 mm × 0.14 mm was selected and the determination of the crystal was carried out on a Siemens Smart CCD diffractometer with a monochromate Mo-Kα radiation ($\lambda = 0.71073$ Å). Intensity data were obtained in the range $2.17^{\circ} \le \theta \le 26.51^{\circ}$ at 293(15) K using ω-scan technique. Corrections for *Lp* factor and empirical absorption correction were applied. The structure was resolved by direct methods. All collected points were used in the structure analysis. All non-hydrogen atoms were determined with successive difference Fourier syntheses and refined with anisotropic thermal parameters by full-matrix least-squares of F^2. All hydrogen atoms were located at calculated positions. All calculations were performed on a computer with SHELX-97 package [9].

3. Results and discussion

3.1. *Descriptions of structure*

Crystal data and structure refinement parameters are listed in table 1. Selected bond lengths and angles are given in table 2. The molecular structure of the title complex is shown in figure 1. In **1**, Cd(II) is six-coordinate, octahedral with four nitrogen atoms from two phen ligands and two oxygen atoms from carboxylate of suberate ligands. The average bond distances are Cd–N, 2.452 Å and Cd–O, 2.337 Å. The dihedral angle of two phen planes is 86.5°, almost vertical. N(1), N(1A), N(2A), and O(2) are in the equatorial plane while N(2) and O(2A) occupy axial positions. The bond angle N(2)–Cd(1)–O(2A) is 166.61° indicating the octahedron is greatly distorted. A 1-D zigzag chain is ultimately formed by bridging carboxylates suberate.

Table 1. Crystal data and structure refinement for $\{[Cd(phen)_2(sube)]\cdot H_2O\}_n$.

Molecular formula	$C_{32}H_{32}CdN_4O_6$
Molecular weight	681.02
Molecular size $(mm)^3$	0.20 × 0.18 × 0.14
Molecular color	Colorless
Crystal system	Monoclinic
Space group	$C2/c$
a (Å)	10.880(4)
b (Å)	19.958(6)
c (Å)	13.511(4)
β	101.981(5)
V	2869.9(16)
Z	4
D_c	1.576
$F(000)$	1392
Absorption correction T_{max}/T_{min}	1.0000/0.707309
Goodness-of-fit on F^2	1.031
Absorption coefficient (mm^{-1})	0.814
Largest diff. peak and hole $(e\,Å^{-3})$	0.327/−0.38
Data/restraints/parameters	2955/0/195
R_1, $wR_2[I>2\sigma(I)]$	0.0337, 0.0656
R_1, wR_2 (all data)	0.0506, 0.0704

Table 2. Selected bond lengths (Å) and angles (°) for $\{[Cd(phen)_2(sube)]\cdot H_2O\}_n$.

Bond distances (Å)			
Cd(1)–O(2)#1	2.337(2)	Cd(1)–N(1)	2.465(2)
Cd(1)–O(2)	2.337(2)	O(1)–C(25)	1.217(4)
Cd(1)–N(2)	2.438(2)	O(2)–C(25)	1.246(3)
Cd(1)–N(2)#1	2.438(2)	C(28)–C(28)#2	1.526(6)
Cd(1)–N(1)#1	2.465(2)		
Bond angles (°)			
O(2)#1–Cd(1)–O(2)	94.30(13)	N(2)#1–Cd(1)–N(1)#1	67.53(8)
O(2)#1–Cd(1)–N(2)	166.61(8)	O(2)#1–Cd(1)–N(1)	125.22(8)
O(2)–Cd(1)–N(2)	92.03(9)	O(2)–Cd(1)–N(1)	80.30(8)
O(2)#1–Cd(1)–N(2)#1	92.03(9)	N(2)–Cd(1)–N(1)	67.53(8)
O(2)–Cd(1)–N(2)#1	166.61(8)	N(2)#1–Cd(1)–N(1)	86.41(8)
N(2)–Cd(1)–N(2)#1	84.33(11)		

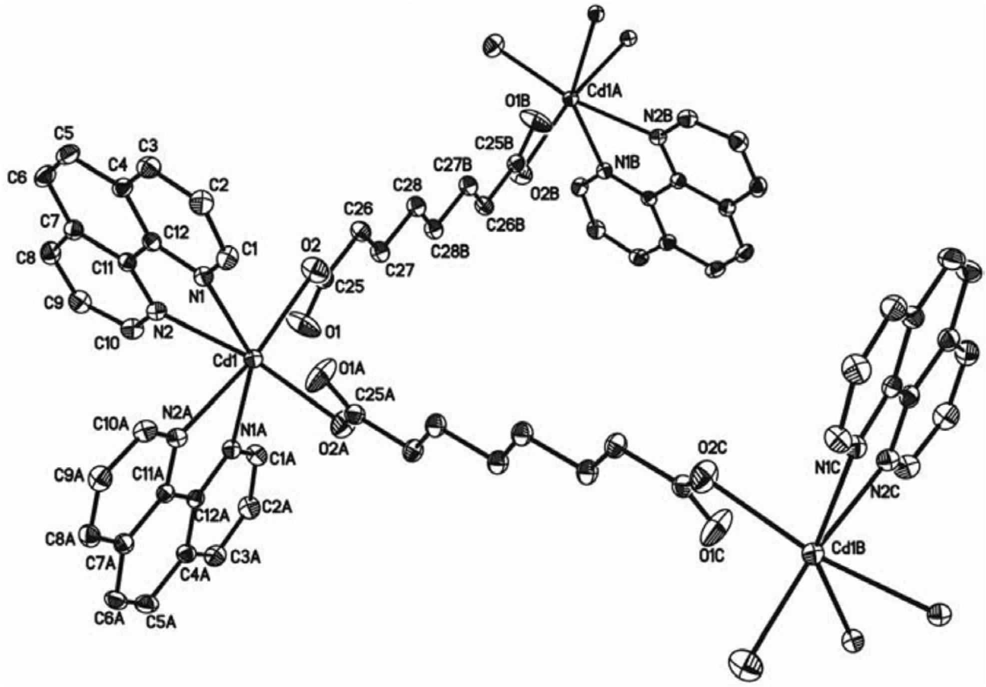


Figure 1. The coordination environment of cadmium in **1**.

Intriguing structure motifs are important for supermolecular chemistry [10]. Interpenetrating framework complexes including (4,4)nets [11], (6,3)nets [12], (10,3)nets [13] and (8,3)nets [14] have been reported; these interpenetrating frameworks were constructed by covalent bonds or hydrogen bonds [10]. Interestingly, **1** contains (4,4)nets whose connected nodes are provided by π–π stacking (distance of 3.786 Å) between the phens of neighboring chains, so a 2-D framework structure is formed, as shown in figure 2. The two independent and identical (4,4) networks are inclined so that each is able to pass through the other once. This interpenetration mode is shown in scheme 1. Zheng *et al.* [15] has reported the complex [Cd(sube)(H_2O)$_2$] (**2**), which only formed a 1-D chain structure. So π–π stacking interactions play a crucial role in the 2-D interpenetrating framework of **1**. Wang *et al.* [16] reported $\{Cd[O_2C(CH_2)_4CO_2][phen]\}_n$ (**3**), but the 2-D structure of **1** is also different from **3**, perhaps because **3** was synthesized by hydrothermal methods.

3.2. *IR spectrum*

Peaks at 1510(s) cm^{-1} and 1411(s) cm^{-1} could be attributed to stretching of –N=C– in phen ligand. Two characteristic adsorption peaks of COO^- are $\upsilon_{as}(COO^-)$ 1570 cm^{-1} and $\upsilon_s(COO^-)$ 1364 cm^{-1}. Generally, coordination modes of carboxyl acid could be extracted from the difference between υ_{as} and υ_s [17]. Being larger than 200 cm^{-1} indicates monodentate coordination of COO^-. On the contrary, being less than 200 cm^{-1} suggests a bidentate coordination. In the present work, the difference of

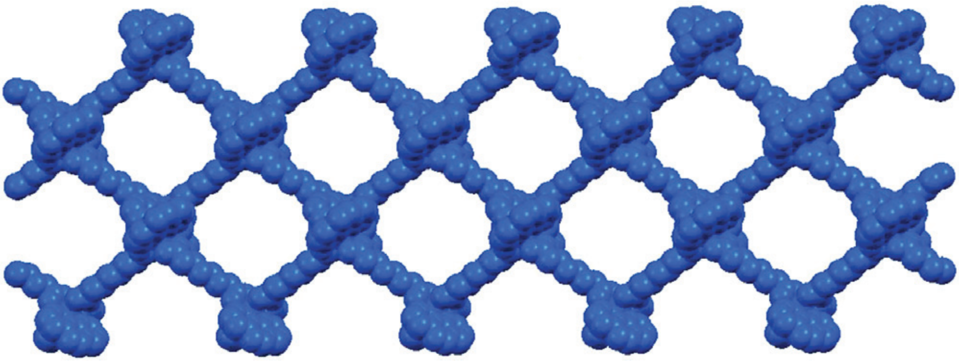
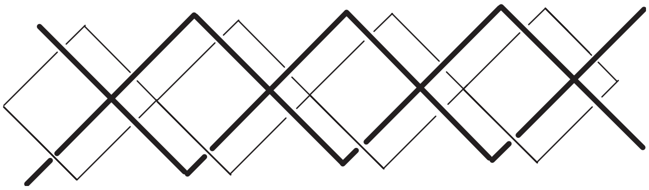


Figure 2. The 2D framework formed through strong π–π stacking interactions (uncoordinated water molecules were omitted for clarity).



Scheme 1. (4,4) networks and twofold interpenetrating manner.

206 cm^{-1} indicates that the suberate ligand is monodentate, consistent with the crystal structural analysis.

3.3. *Thermal analyses*

The TG curve of $\{[Cd(phen)_2(sube)] \cdot 2H_2O\}_n$ shows weight loss of 2.75% from 90 to 120°C corresponding to loss of uncoordinated water (Calcd: 2.65%). Upon further heating, an obvious weight loss (78.38%) occurs in the temperature range 160°C, corresponding to the release of organic ligands (Calcd: 78.50%). After 305°C no weight loss is observed, indicating complete decomposition of $\{[Cd(phen)_2(sube)] \cdot H_2O\}_n$. The residual weight 18.67% (calcd: 18.85%) corresponds to CdO.

3.4. *Photoluminescent properties*

The d^{10} metal compounds have been shown to exhibit interesting photoluminescent properties [18]. The solid-state photoluminescent spectra of **1** at room temperature are depicted in figure 3. **1** exhibits an intense emission maximum at 568 nm in the blue region upon excitation at 398 nm. We further measured the emission spectrum of free suberic acid, which shows one emission at 482 nm upon excitation at 400 nm, indicating that the suberic acid has no emission in the visible region, but when it is bound to a cadmium center, blue luminescence is observed. According to previous reports [19–21], emission bands could be assigned to ligand-to-metal charge transfer (LMCT).

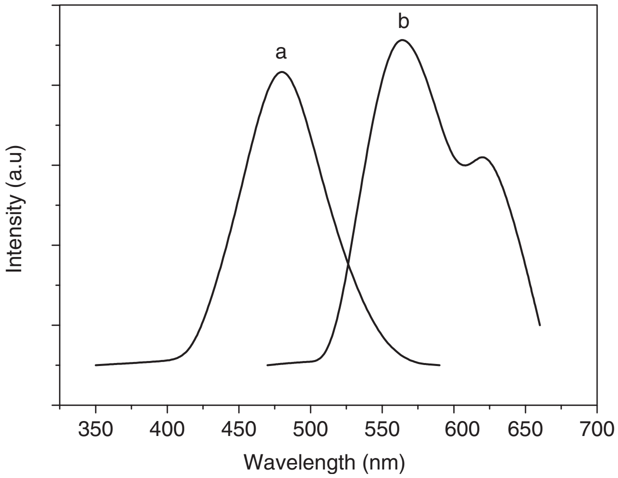


Figure 3. Solid state emission spectra at room temperature (line a is emission spectrum of free suberic acid; line b is emission spectrum of **1**).

4. Conclusions

In this article, we synthesized and structurally characterized a 2-D interpenetrating coordination polymer $\{[\mathrm{Cd(phen)_2(sube)}]\cdot 2\mathrm{H_2O}\}_n$ containing suberate ligands. This work proves that π–π stacking interactions play an important role in interpenetrating framework. The solid state luminescence indicates this coordination polymer may be a candidate for photoactive materials.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 294145. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK (Fax: C44 1223/336 033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Natural Science Foundation of China (No. 20671064) and the Doctor Foundation of Shenyang Institute of Chemical Technology (No. 2006518).

References

[1] S. Leininger, B. Olenyuk, P.J. Stang. *Chem. Rev.*, **100**, 853 (2000).
[2] B. Zhao, P. Cheng, X.Y. Chen, C. Cheng, W. Shi, D.Z. Liao, S.P. Yan, Z.H. Jiang. *J. Am. Chem. Soc.*, **126**, 3012 (2004).

[3] B. Chen, M. Eddaoudi, S.T. Hyde, M. O'Keeffe, O.M. Yaghi. *Science*, **291**, 1021 (2001).
[4] Q.R. Fang, G.S. Zhu, M. Xue, J.Y. Sun, F.X. Sun, S.L. Qiu. *Inorg. Chem.*, **45**, 3582 (2006).
[5] B. Zhao, P. Cheng, Y. Dai, C. Cheng, D.Z. Liao, S.P. Yan, Z.H. Jiang, G.L. Wang. *Angew. Chem. Int. Ed. Engl.*, **42**, 934 (2003).
[6] Y.C. Liang, M.C. Hong, W.P. Su, R. Cao, W.J. Zhang. *Inorg. Chem.*, **40**, 4574 (2001).
[7] (a) D. Braga, S.L. Giaffreda, F. Grepioni. *Chem. Commun.*, 3877 (2006); (b) L.D.T. De, N.S. Gunning, C.L. Cahill. *Inorg. Chem.*, **44**, 258 (2005).
[8] (a) S. Konar, E. Zangrando, M.G.B. Drew, J. Ribas, N.R. Chaudhuri. *Dalton Trans.*, 260, (2004); (b) G.Q. Zhang, G.Q. Yang, J.S. Ma. *Cryst. Growth Des.*, **6**(4), 933 (2006).
[9] (a) G.M. Sheldrick. *SHELXS-97, Crystal Structure Solution*, Göttingen University, Germany (1997); (b) G.M. Sheldrick. *SHELXS-97, Program for X-ray Crystal Structure Refinement*, Göttingen University, Germany (1997).
[10] S.R. Batten, R. Robson. *Angew. Chem. Int. Ed. Engl.*, **37**, 1460 (1998).
[11] S.B. Copp, S. Subramanian, M.J. Zaworotko. *Angew. Chem. Int. Ed. Engl.*, **32**, 706 (1993).
[12] S.R. Batten, B.F. Hoskins, R. Robson. *New. J. Chem.*, **22**, 173 (1998).
[13] 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. Engl.*, **43**, 990 (2004).
[14] X. Cieren, J. Angenault, J.-C. Courtier, S. Jaulmes, M. Quarton, F. Robert. *J. Solid State Chem.*, **121**, 230 (1996).
[15] Y.Q. Zheng, J. Sun, J.L. Lin. *Z. Anorg. Allg. Chem.*, **627**, 90 (2001).
[16] N. Hao, E.H. Shen, Y.G. Li, E.B. Wang, C.W. Hu, L. Xu. *Eur. J. Inorg. Chem.*, **2004**, 4102 (2004).
[17] G.B. Deacon, R. Phillips. *J. Coord. Chem. Rev.*, **33**, 227 (1980).
[18] S.A. Bourne, J.J. Lu, A. Mondal, B. Moulton, M.J. Zaworotko. *Angew. Chem. Int. Ed.*, **40**, 2111 (2001).
[19] J. Tao, M.L. Tong, J.-X. Shi, X.-M. Chen, S.W. Ng. *Chem. Commun.*, 2043 (2000).
[20] R. Bertoncell, M. Bettinelli, M. Cassrin, A. Gulino, E. Tondello, A. Vittadini. *Inorg. Chem.*, **31**, 1558 (1993).
[21] Z.-Y. Fu, S.M. Hu, J.-C. Dai, J.-J. Zhang, X.-T. Wu. *Eur. J. Inorg. Chem.*, **2003**, 2670 (2003).