

Synthesis and Crystal Structure of a 2-D Framework Supramolecular Complex $[\text{Cd}_2(\text{phen})_2(\text{adip})(\text{NO}_3)_2]$

SUN Ya-Guang^{a, b} GAO En-Jun^a
WEI De-Zhou^b WANG Chuan-Sheng^a

^a(Laboratory of Coordination Chemistry, Shenyang
Institute of Chemical Technology, Shenyang 110142, China)

^b(School of Resource & Civil Engineering, Northeastern University, Shenyang 110004, China)

ABSTRACT A novel binucleus complex $[\text{Cd}_2(\text{phen})_4(\text{adip})(\text{NO}_3)_2]$ (phen = phenanthroline, H_2adip = adipic acid) has been synthesized by the reaction of phen and H_2adip with cadmium(II) salt. Elemental analysis, IR spectra and X-ray crystal structure analysis were carried out to determine the crystal structure of the title complex. The crystal belongs to triclinic, space group $P\bar{1}$ with $a = 9.638(7)$, $b = 10.315(7)$, $c = 13.109(10)$ Å, $\alpha = 88.305(11)$, $\beta = 69.011(11)$, $\gamma = 75.818(11)^\circ$, $\text{C}_{27}\text{H}_{20}\text{N}_5\text{O}_5\text{Cd}$, $M_r = 606.88$, $Z = 2$, $V = 1177.2(14)$ Å³, $D_c = 1.712$ g/cm³, $\mu = 0.979$ mm⁻¹, -8 h 11 , -12 k 12 , -10 l 15 , $F(000) = 610$, $R_{\text{int}} = 0.0314$, $R = 0.0739$ and $wR = 0.1922$ ($I > 2\sigma(I)$). The cadmium atom is seven-coordinated in a distorted pentagonal bipyramidal configuration. The complex forms a 2-D supramolecular framework by C-H...O weak interactions and π - π stacking of neighbouring phen ligands.

Keywords: cadmium(II), supramolecular, adipic acid, crystal structure

1 INTRODUCTION

In the design of crystal molecule, inorganic crystal engineering is one of the focused fields that are ever developing^[1]. The introduction of different metal ions and bridging ligands often gives rise to novel physical and chemical properties^[2-4]. Consequently, the supramolecular compounds constructed from weak interactions, such as hydrogen bond, π - π stacking, C-H...O interaction, ion- π interaction and hydrophobic interaction, have become the new focus of crystal engineering field^[5]. In particular, due to the potential application in optical materials, supramolecular compounds with d^{10} metal ions have captured the interest of chemists^[6, 7]. There have been extensive studies about the supramolecular

complexes that constructed from the reaction of Cd(II) and Zn(II) with di-, tri- or tetra-aromatic carboxylic acid possessing rigid structures these years^[8-10]. Because of carboxylic acid ligands have versatile types and coordination modes, there are still many things to be done to reveal the supramolecular chemistry of metal-carboxylic acid system. Herein, by using adipic acid (H_2adip) as bridging ligand and 1,10-phenanthroline (phen) as terminal ligand, we successfully synthesized a novel binucleus complex $[\text{Cd}_2(\text{phen})_4(\text{adip})(\text{NO}_3)_2]$. X-ray structural analysis shows that the complex forms a 2-D supramolecular framework through C-H...O weak interactions and π - π stacking of neighbouring phen ligands.

Received 23 September 2005; accepted 23 October 2005 (CCDC 283844)

This work was supported by the Foundation of Education Committee of Liaoning Province (No. 2004c021) and Foundation of Excellent Personal of Shenyang Institute of Chemical Technology
Corresponding author. E-mail: ejgao@yahoo.com.cn

2 EXPERIMENTAL

2.1 Reagents and physical measurements

All chemicals of reagent grade were obtained from commercial sources and used without further purification. C, H and N analyses were carried out with a Finnigan EA 1112 element analyzer. IR spectra were performed on a Nicolet470 spectrometer with KBr pellets in the 4000~400 cm^{-1} region. The crystal determination was recorded on a Siemens Smart CCD diffractometer. Structure analysis was performed on a computer with SHELX-97 program package.

2.2 Synthesis of the title compound

0.1 mmol adipic acid was dissolved in 10 mL water. Then the resultant solution was mixed with 20 mL ethanol containing 0.2 mmol phen. Under the condition of stirring, 10 mL water containing 0.1 mmol $\text{Cd}(\text{NO}_3)_2$ was added slowly. During this time, the pH of the solution decreased gradually, and 0.5 mol/L KOH solution was used to adjust the pH to 8.547. Kept stirring for about 5 h till the pH value was stable at 7.862. After the solution was condensed with a rotatory evaporator, 35 mL condensed colorless transparent liquid was kept under room temperature for 10 days to give colorless transparent crystals. Anal. Calcd. (%) for $\text{C}_{27}\text{H}_{20}\text{N}_5\text{O}_5\text{Cd}$: C, 55.84; H, 4.28; N, 7.38. Found (%): C, 56.04; H, 4.43; N, 7.47. IR (cm^{-1}): 3064(m), 1550(s), 1517(s), 1429(s), 1358(s), 1335(s), 844(s), 727(s).

2.3 X-ray structure determination

A colorless single crystal with dimensions of 0.40mm \times 0.20mm \times 0.18mm was selected and the crystal determination was carried out on a Siemens Smart CCD diffractometer with a molybdenum-mo-
nochromate $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by using an ω -scan technique in the range of 1.67θ 25.00° at 294(2) K. A total of 5923 reflections were collected, of which 4000 ($R_{\text{int}} = 0.0314$) were inde-

pendent and 3568 were observed with $I > 2\sigma(I)$. The correction for Lp factors and empirical absorption correction were applied. The structure was solved by direct methods. All the 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 on F^2 . All hydrogen atoms were located at the calculated positions. All calculations were performed on a computer with SHELX-97 program package^[11, 12]. The final refinement converged at $R = 0.0737$, $wR = 0.1922$ ($w = 1/[\sigma^2(F_o^2) + (0.0760P)^2 + 12.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$), $(\Delta/\sigma)_{\text{max}} = 0.001$, $S = 1.085$, $(\Delta\rho)_{\text{max}} = 3.278$ and $(\Delta\rho)_{\text{min}} = -1.327 \text{ e/\AA}^3$.

3 RESULTS AND DISCUSSION

3.1 IR spectra

Peaks at 1517(s) and 1429(s) cm^{-1} could be attributed to the stretching vibration of $-\text{N}=\text{C}-$ in phen ligand. Two characteristic adsorption peaks of COO^- are $\nu_{\text{as}}(\text{COO}^-)$ 1550 cm^{-1} and $\nu_{\text{s}}(\text{COO}^-)$ 1358 cm^{-1} . Generally, coordination modes of carboxyl acid could be extracted from the peak value difference between ν_{as} and ν_{s} ^[13]. Being larger than 200 cm^{-1} indicates the monodentate coordination mode of COO^- group, on the contrary, being less than 200 cm^{-1} suggests a bidentate coordination mode. In the present work, the difference 192 cm^{-1} indicates that the adipic acid adopts a bidentate coordination mode, which is consistent with the single crystal structural analysis.

3.2 Crystal structure

The atomic coordinates and thermal parameters of non-hydrogen atoms are listed in Table 1, and the selected bond lengths and bond angles in Table 2. The molecular structure of the title complex is shown in Fig. 1.

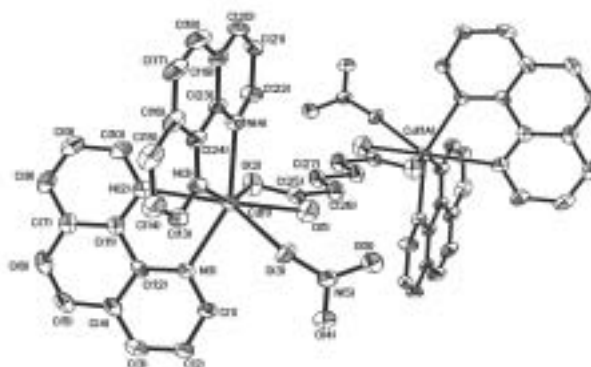
Table 1. Non-hydrogen Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\text{\AA} \times 10^3$) for $[\text{Cd}_2(\text{phen})_2(\text{adip})(\text{NO}_3)_2]$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}	Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Cd(1)	4838(1)	7594(1)	2606(1)	37(1)	C(13)	7142(11)	9471(10)	1480(8)	47(2)
O(1)	2281(8)	7934(7)	3361(6)	59(2)	C(14)	8211(12)	10182(11)	1358(9)	55(3)
O(2)	3464(8)	5907(7)	3509(6)	59(2)	C(15)	8683(12)	10335(10)	2217(10)	59(3)
N(1)	5501(8)	6943(7)	764(5)	34(2)	C(16)	8034(11)	9770(9)	3206(9)	47(2)
N(2)	7039(9)	5674(7)	2050(6)	43(2)	C(17)	8383(12)	9938(10)	4155(10)	56(3)
N(3)	6534(8)	8901(7)	2392(6)	38(2)	C(18)	7723(13)	9420(10)	5092(10)	56(3)
N(4)	5304(9)	7728(7)	4276(6)	39(2)	C(19)	6679(11)	8638(9)	5152(8)	43(2)
C(1)	4770(11)	7555(9)	146(7)	38(2)	C(20)	5999(12)	8006(10)	6115(8)	50(2)
C(2)	5056(11)	7107(10)	-912(7)	45(2)	C(21)	5054(11)	7255(10)	6115(8)	49(2)
C(3)	6193(12)	5965(10)	-1348(8)	51(2)	C(22)	4729(12)	7121(10)	5170(8)	47(2)
C(4)	7007(11)	5284(9)	-726(7)	42(2)	C(23)	6295(10)	8443(8)	4248(7)	36(2)
C(5)	8220(12)	4101(10)	-1125(8)	54(3)	C(24)	6970(10)	9054(8)	3254(8)	36(2)
C(6)	8991(12)	3493(10)	-492(9)	56(3)	C(25)	2259(11)	6795(9)	3713(7)	40(2)
C(7)	8652(11)	4011(9)	587(8)	46(2)	C(26)	733(11)	6525(10)	4384(8)	49(2)
C(8)	9475(12)	3428(10)	1251(10)	57(3)	C(27)	781(10)	5089(10)	4652(8)	47(2)
C(9)	9056(13)	3958(11)	2280(10)	59(3)	N(5)	2517(9)	677(8)	1870(6)	43(2)
C(10)	7817(12)	5071(10)	2657(9)	51(2)	O(3)	3736(7)	28(7)	1959(6)	51(2)
C(11)	7465(10)	5158(8)	1013(7)	36(2)	O(4)	2213(9)	497(9)	1057(6)	68(2)
C(12)	6616(9)	5832(8)	349(6)	34(2)	O(5)	1601(10)	1527(8)	2604(7)	72(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. Selected Bond Lengths (\AA) and Bond Angles ($^\circ$) for $[\text{Cd}_2(\text{phen})_2(\text{adip})(\text{NO}_3)_2]$

Bond	Dist.	Bond	Dist.	Bond	Dist.
Cd(1)–O(1)	2.242(7)	Cd(1)–N(1)	2.339(7)	O(1)–C(25)	1.251(11)
Cd(1)–O(2)	2.463(7)	Cd(1)–N(2)	2.423(8)	O(2)–C(25)	1.238(11)
Cd(1)–N(4)	2.401(7)	Cd(1)–N(3)	2.301(7)		
Angle	($^\circ$)	Angle	($^\circ$)	Angle	($^\circ$)
O(1)–Cd(1)–N(3)	134.9(3)	O(1)–Cd(1)–N(2)	136.4(3)	N(3)–Cd(1)–O(2)	153.9(3)
O(1)–Cd(1)–N(1)	105.8(3)	N(3)–Cd(1)–N(2)	87.3(3)	N(1)–Cd(1)–O(2)	100.7(3)
O(1)–Cd(1)–N(4)	97.3(3)	N(1)–Cd(1)–N(2)	70.0(3)	N(4)–Cd(1)–O(2)	84.5(3)
N(3)–Cd(1)–N(1)	98.6(2)	O(1)–Cd(1)–O(2)	54.5(2)	O(2)–Cd(1)–N(2)	83.0(3)
N(4)–Cd(1)–N(3)	70.6(3)	N(1)–Cd(1)–N(4)	154.9(3)		

**Fig. 1. Molecular structure of complex $[\text{Cd}_2(\text{phen})_2(\text{adip})(\text{NO}_3)_2]$**

As shown in Fig. 1, Cd(II) presents a seven- coordinated pentagonal bipyramid geometry with four nitrogen atoms from two phen ligands, two carboxyl

oxygen atoms from adipic acid and one oxygen atom from nitrate ion. In detail, N(2), N(3), O(1), O(2) and O(3) locate at the equatorial plane. The sum of

five angles (O(3)–Cd(1)–N(3) 70.38°, O(3)–Cd(1)–O(1) 75.85°, O(1)–Cd(1)–O(2) 54.47°, O(2)–Cd(1)–N(4) 84.53°, N(3)–Cd(1)–N(4) 70.62°) is 355.85°, which is 4.15° less than the expectation value 360°. N(1) and N(4) occupy the axial positions. The bond angle of N(1)–Cd(1)–N(4) is 154.83°, indicating the pentagonal bipyramid is distorted greatly. The binucleus structure is ultimately formed by the bridge nature of carboxyl acid group in adipic acid.

The title compound features C–H···O weak interactions between terminal oxygen atom of nitrate and phen ring in the adjacent molecules (H···O distances are 2.464 and 2.563 Å, C–H···O are 134.80 and 157.33°, respectively). Upon this weak interaction, a quasi-square arrangement is generated by four Cd ions of two discrete binucleus coordination molecules. As shown in Fig. 2, the distance between

two Cd ions located at square's diagonal is 18 Å. Furthermore, a ladder-like structure is formed by this square arrangement with the presence of weak interactions. It is interesting to mention that the Cd ions located at the two chains of ladder are coplanar severely, which is different with those in [Cu(phen)₂(C₆H₈O₄)]·4.5H₂O and [(Cu₂(phen)₂Cl₂)(C₆H₈O₄)]·4H₂O (Zhen *et al.*)^[14] to some extent. The C–H···O weak interactions could also be found among chains (H···O distances are 2.647, 2.586 and 2.623 Å, C–H···O are 142.32, 143.66 and 141.63°, respectively). Besides, from Fig. 3, π - π stacking among adjacent phen rings also exists with distances of mass center ranging from 3.650 to 3.772 Å. As shown in Fig. 4, a two-dimensional network is ultimately constructed through C–H···O weak interactions and π - π stacking.

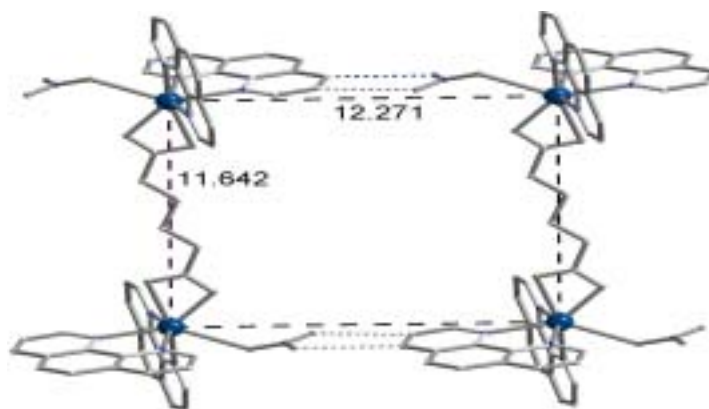


Fig. 2. Square structure formed by C–H···O weak interactions of cadmium ions (Hydrogen atoms are omitted for clarity)

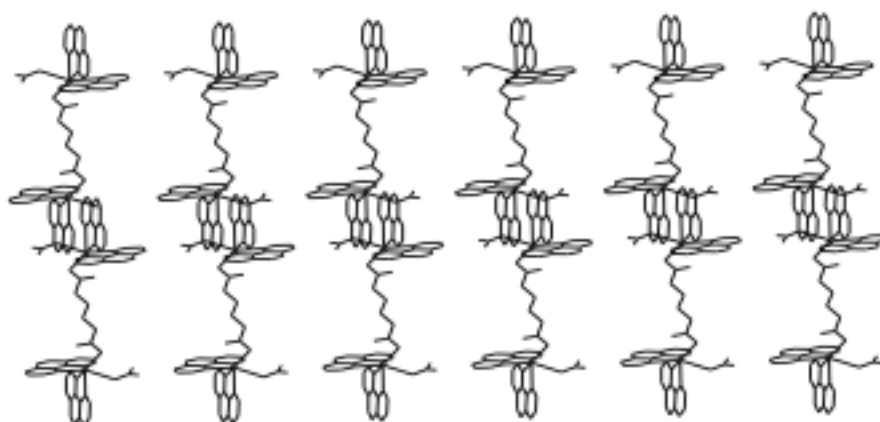


Fig. 3. π - π stacking interactions of neighbouring molecules (hydrogen atoms are omitted for clarity)

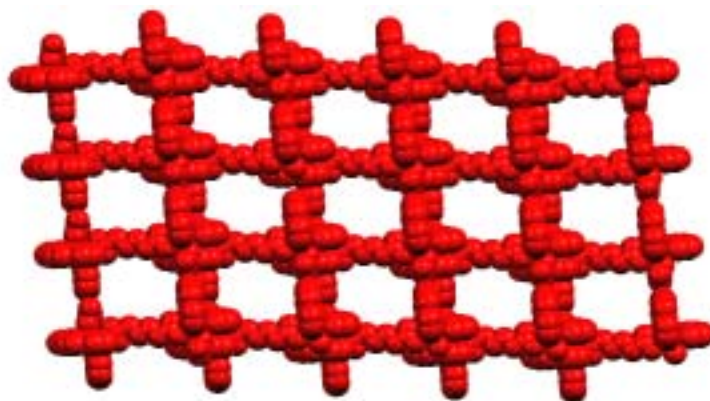


Fig. 4. 2D framework of complex $[\text{Cd}_2(\text{phen})_2(\text{adip})(\text{NO}_3)_2]$

REFERENCES

- (1) Brian, M.; Michael, J. Z. *Chem. Rev.* **2001**, 101, 1629–1658.
- (2) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O’Keeffe, M.; Yaghi, O. M. *Science* **2003**, 300, 1127–1129.
- (3) Zhou, Y. F.; Jiang, F. L.; Yuan, D. Q.; Wu, B. L.; Wang, R. H.; Lin, Z. Z.; Hong, M. C. *Angew. Chem. Int. Ed.* **2004**, 43, 5665–5668.
- (4) Zhao, B.; Cheng, P.; Chen, X. Y.; Cheng, C.; Shi, W.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H. *J. Am. Chem. Soc.* **2004**, 126, 3012–3013.
- (5) Liu, Q. T.; Guan, W.; Sun, J. Y.; Zhang, X. D. *Chin. Chem. Bull.* **1998**, 7, 21–26.
- (6) Tong, M. L.; Chen, X. M.; Ye, B. H.; Ji, L. N. *Angew. Chem. Int. Ed.* **1999**, 38, 2237–2240.
- (7) Bourne, S. A.; Lu, J. J.; Mondal, A.; Moulton, B.; Zaworotko, M. J. *Angew. Chem. Int. Ed.* **2001**, 40, 2111–2113.
- (8) Chen, J. X.; Liu, S. X. *Chin. J. Stru. Chem.* **2005**, 24, 54–58.
- (9) Gao, H. L.; Ding, B.; Yi, L.; Cheng, P.; Liao, D. Z.; Yan, S. P.; Jiang, Z. H. *Inorg. Chem. Commun.* **2005**, 8, 151–154.
- (10) Dai, J. C.; Wu, X. T.; Fu, Z. Y.; Cui, C. P.; Hu, S. M.; Du, W. X.; Wu, L. M.; Zhang, H. H.; Sun, R. M. *Inorg. Chem.* **2002**, 41, 1391–1396.
- (11) Sheldrick, G. M. *SHELXS-97, Program For X-ray Crystal Structure Solution*, Göttingen University, Germany **1997**.
- (12) Sheldrick, G. M. *SHELXS-97, Program For X-ray Crystal Structure Refinement*, Göttingen University, Germany **1997**.
- (13) Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, 33, 227–250.
- (14) Zheng, Y. Q.; Sun, J.; Lin, J. L. *Z. Anorg. Allg. Chem.* **2001**, 627, 90–94.