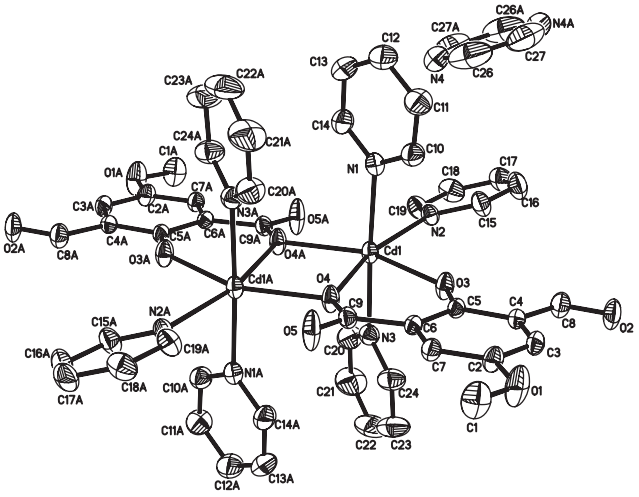
Xue L. Niu and Hua Yang*

Crystal structure of bis(μ$_2$-3-formyl-5-methoxy-2-oxidobenzoato-κ^3*O*,*O*′:*O*′)-hexapyridine-dicadmium(II) – pyridine (1/1), $C_{53}H_{47}Cd_2N_7O_{10}$



https://doi.org/10.1515/ncrs-2018-0108
Received April 12, 2018; accepted June 27, 2018; available online July 13, 2018

Abstract

$C_{53}H_{47}Cd_2N_7O_{10}$, triclinic, $P\bar{1}$, $a = 9.6670(9)$ Å, $b = 10.5089(11)$ Å, $c = 13.2081(12)$ Å, $\alpha = 109.879(2)°$, $\beta = 97.894(1)°$, $\gamma = 92.201(1)°$, $V = 1244.7(2)$ Å^3, $Z = 1$, $R_{gt}(F) = 0.0388$, $wR_{ref}(F^2) = 0.0926$, $T = 298(2)$ K.

CCDC no.: 1822732

Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

2-Hydroxy-3-carboxyl-5-methoxybenzaldehyde (0.0420 g, 0.2 mmol) was dissolved in pyridine (10 mL). $Cd(NO_3)_2{\cdot}4\ H_2O$ (0.0925 g, 0.3 mmol) was added. After stirring for 30 min at room temperature, 10 drops methanol solution of tetramethylammonium hydroxide (*w*/*w*: 25%) was added. After further stirring for 5 h, the filtrate was divided into three test tubes, and then slowly dripped into ethanol and ether, which resulted in a distinct stratification between the solution and diffusion. After 2 weeks, yellow block crystal were obtained. The 0.0267 g of product represents a yield of 15.26%. The m.p. was measured at >573 K. **Elemental analysis**: Found: C, 52.89; H, 3.88; N, 8.13. Calcd. For $C_{53}H_{47}Cd_2N_7O_{10}$: C, 54.50; H, 4.02; N. 8.40%; IR (cm^{-1}): 3441(*s*), 1674(*m*), 1575(*m*), 1427(*s*), 1006(*m*), 795.7(*s*).

Table 1: Data collection and handling.

Crystal:	Yellow massive
Size:	0.41 × 0.21 × 0.18 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	0.92 mm^{-1}
Diffractometer, scan mode:	APEX, φ and ω
θ_{max}, completeness:	25.0°, 95%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6240, 4290, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3347
$N(param)_{refined}$:	326
Programs:	SHELX [15], Bruker [16]

Experimental details

H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and $U_{iso}(H) = 1.2\ U_{eq}(C)$, respectively [15]. The highest peak is located 0.361 Å from Cu1.

Comment

Carboxylate ligands play important roles in construction of metal complexes in the coordination chemistry due to their distinctive structural features, such as multidonors [1, 2]. Complexes involving the carboxylates are mainly focused on transition and lanthanide metal centers, while the cadmium complexes are rarer. Some cadmium complexes also show properties, such as luminescence [3–10], antimicrobial [11, 12], electrocatalytic [13] and spectroscopic ones

***Corresponding author: Hua Yang,** Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, Department of Chemistry and Chemical Engineering, Liaocheng University, Shandong 252059, China, e-mail: yanghua_1101@163.com
Xue L. Niu: Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, Department of Chemistry and Chemical Engineering, Liaocheng University, Shandong 252059, China; and Jincheng Institute of Technology, Shanxi 048026, China

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
Cd1	0.63714(3)	0.51612(3)	0.61692(2)	0.03651(13)
N1	0.5639(4)	0.7307(4)	0.7156(3)	0.0425(9)
N3	0.7181(4)	0.3030(4)	0.5259(3)	0.0431(9)
O3	0.5589(3)	0.4220(3)	0.7278(2)	0.0497(8)
O4	0.4080(3)	0.4306(3)	0.5346(2)	0.0464(8)
C5	0.4392(4)	0.3779(4)	0.7395(3)	0.0326(9)
N2	0.8459(4)	0.5826(3)	0.7407(3)	0.0384(8)
C7	0.1868(5)	0.3155(4)	0.6890(3)	0.0380(10)
H7	0.1041	0.3069	0.6410	0.046*
O2	0.5624(4)	0.3174(4)	0.9878(3)	0.0649(10)
O5	0.1828(4)	0.3832(4)	0.5083(3)	0.0760(12)
C14	0.5947(6)	0.8416(5)	0.6944(4)	0.0641(15)
H14	0.6475	0.8356	0.6394	0.077*
C9	0.2977(5)	0.3929(4)	0.5632(3)	0.0373(10)
O1	0.0617(4)	0.2368(4)	0.8080(3)	0.0765(12)
C6	0.3108(4)	0.3608(4)	0.6659(3)	0.0319(9)
C8	0.5543(5)	0.3511(5)	0.9096(4)	0.0501(12)
H8	0.6366	0.3875	0.8969	0.060*
C4	0.4285(4)	0.3408(4)	0.8325(3)	0.0348(10)
C1	−0.0658(5)	0.2324(6)	0.7467(5)	0.0723(16)
H1A	−0.0806	0.3212	0.7443	0.108*
H1B	−0.1386	0.2033	0.7788	0.108*
H1C	−0.0677	0.1696	0.6740	0.108*
C13	0.5520(7)	0.9651(6)	0.7502(5)	0.0798(19)
H13	0.5741	1.0409	0.7323	0.096*
C3	0.3024(5)	0.2960(4)	0.8521(3)	0.0420(11)
H3	0.2994	0.2746	0.9146	0.050*
C24	0.6580(6)	0.1920(5)	0.5325(4)	0.0620(14)
H24	0.5840	0.2002	0.5719	0.074*
C2	0.1825(5)	0.2829(4)	0.7810(4)	0.0429(11)
C12	0.4769(7)	0.9760(6)	0.8323(5)	0.0727(16)
H12	0.4476	1.0590	0.8719	0.087*
C23	0.6992(7)	0.0647(6)	0.4841(6)	0.086(2)
H23	0.6547	−0.0115	0.4906	0.103*
C10	0.4916(5)	0.7442(5)	0.7962(4)	0.0518(12)
H10	0.4710	0.6677	0.8137	0.062*
C19	0.696(5)	0.5995(5)	0.7132(4)	0.0523(12)
H19	0.9732	0.5903	0.6411	0.063*
C11	0.4460(6)	0.8630(5)	0.8547(4)	0.0651(15)
H11	0.3939	0.8668	0.9096	0.078*
C15	0.8446(5)	0.5963(5)	0.8445(4)	0.0562(13)
H15	0.7588	0.5836	0.8656	0.067*
C20	0.8240(6)	0.2892(5)	0.4711(4)	0.0658(15)
H20	0.8682	0.3665	0.4660	0.079*
C22	0.8064(8)	0.0535(7)	0.4269(6)	0.097(2)
H22	0.8353	−0.0313	0.3913	0.116*
C17	1.0888(6)	0.6434(5)	0.8903(4)	0.0681(16)
H17	1.1710	0.6631	0.9406	0.082*
C18	1.0926(5)	0.6298(5)	0.7846(4)	0.0618(14)
H18	1.1774	0.6408	0.7614	0.074*
C16	0.9614(6)	0.6276(6)	0.9211(4)	0.0683(16)
H16	0.9552	0.6382	0.9931	0.082*
C21	0.8711(8)	0.1672(7)	0.4219(5)	0.095(2)
H21	0.9473	0.1615	0.3850	0.114*
C26	0.8698(10)	0.9679(7)	0.9618(13)	0.133(4)
H26	0.7739	0.9445	0.9392	0.160*
N4	0.9454(14)	0.9734(10)	0.8935(8)	0.061(3)
H25[a]	0.9103	0.9570	0.8264	0.073*
C27[a]	0.9273(15)	0.9968(8)	1.0739(10)	0.124(3)
H27	0.8682	0.9932	1.1230	0.148*

[a]Occupancy: 0.5.

[14]. Complexes based on the 2-hydroxy-3-hydroxymethyl-5-methoxy-benzoic acid are rare eventhough the anion of this molecule may act as multidonors to coordinate or bridge metal ions. Herein, a dinuclear cadmium complex is reported.

The dinuclear title cadmium complex has a centrosymmetric structure and belongs to a triclinic crystal system. The complex consists of two Cd ions, two deprotoned 2-hydroxy-3-carboxyl-5-methoxybenzaldehyde ligands, six coordinated pyridine molecules. Two Cd ions are linked through the oxygen atom of the carboxyl group with the distance of 3.695 Å. Each Cd ion is located in a deformed octahedral environment with the coordination atoms N_3O_3 from the phenolic hydroxyl group (O3), the carboxyl groups (O4, O4 #) of the ligand, and three coordinated pyridine molecules (N1, N2, N3). The bond lengths Cd—O and Cd—N are 2.221–2.328 Å and 2.335–2.381 Å, respectively. The coordination atoms of each ligand form a stable six-member ring through the Cd ion.

Acknowledgements: We are grateful for financial support of this work from the Natural Science Foundation of China (21701078).

References

1. Zhang, S. W.; Shi, W.; Cheng, P.: The coordination chemistry of *N*-heterocyclic carboxylic acid: a comparison of the coordination polymers. Coord. Chem. Rev. **352** (2017) 108–150.
2. Xiang, S.; Bao, D. X.; Wang, J.; Li, Y. C.; Zhao, X. Q. : Luminescent lanthanide coordination compounds with pyridine-2,6-dicarboxylic acid. J. Lumin. **186** (2017) 273–282.
3. Coropeceanu, E. B.; Croitor, L.; Siminel, A. V.; Fonari, M. S.: Preparation, structural characterization and luminescence studies of mono- and binuclear Zn(II) and Cd(II) acetates with pyridine-4-aldoxime and pyridine-4-amidoxime ligands. Polyhedron **75** (2014) 73–80.
4. Arici, M.; Yesilel, O. Z.; Tas, M.: Cd(II)-coordination polymers based on tetracarboxylic acid and diverse bis(imidazole) ligands: synthesis, structural diversity and photoluminescence properties. J. Solid State Chem. **245** (2017) 146–151.
5. Huang, C. Y.; Wang, J.; Ding, Z. Y.; Cui, K.: Luminescent properties, internal hydrogen bonds and π-π interactions of Cd(II), Zn(II), Co(II) complexes based on 2,8-di(pyridin-4-yl)dibenzothiophene and dicarboxylate ligands. J. Mol. Struct. **1086** (2015) 118–124.
6. Croitor, L.; Coropceanu, E. B.; Siminel, A. V.; Botoshansky, M. M.; Fonari, M. S.: Synthesis, structures, and luminescence properties of mixed ligand Cd(II) and Zn(II) coordination compounds mediated by 1,2-bis(4-pyridyl)ethane. Inorg. Chim. Acta **370** (2011) 411–419.
7. Wang, J. J.; Tang, L.; Zhang, M. L.; Gao, L. J.; Ren, Y. X.; Hou, X. Y.; Fu, F.: Synthesis and characterization of three 2D Cd(II) coordination polymers built with terphenyl-2,2′,4,4′-tetracarboxylate and flexible bis(imidazole). J. Mol. Struct. **1085** (2015) 215–221.
8. Zhang, G. Y.; Zhou, X. L.; Li, T.; Meng, X. R.: Three Cd^{II} complexes based on 2-(1*H*-imidazol-1-methyl)-1*H*-benzimidazole

and homologous aliphatic dicarboxylates. Inorg. Chim. Acta **421** (2014) 45–51.
9. Basak, S.; Sen, S.; Marschner, C.; Baumgartner, J.; Batten, S. R.; Turner, D. R.; Mitra, S.: Synthesis, crystal structures and fluorescence properties of two new di- and polynuclear Cd(II) complexes with N_2O donor set of a tridentate Schiff base ligand. Polyhedron **27** (2008) 1193–1200.
10. Bai, C.; Xu, B.; Hu, H. M.; Yang, M. L.; Xue, G. L.: Cadmium(II) coordination polymers constructed from a bis-functionalized ligand 4′-(3-carboxyphenyl)-2,2′:6′,2″-terpyridine: synthesis, structure and luminescence. Polyhedron **124** (2017) 1–11.
11. Musavi, S. A.; Montazerozohori, M.; Masoudiasl, A.; Naghiha, R.; Joohari, S.; Assoud, A.: Crystal structure, DNA interaction and thermal analysis data of two new antimicrobial active binuclear cadmium and mercury complexes. J. Mol. Struct. **1145** (2017) 65–75.
12. Lei, N.; Ren, Q. L.; Liu, Y. P.; Li, J.; Cong, P.; Qin, J.; Zhu, H. L.: Synthesis, structure, and properties of Cd(II) complexes generated from 2-phenylquinoline derivatives. J. Mol. Struct. **1067** (2014) 220–224.
13. Zhuang, R. R.; Jian, F. F.; Wang, K. F.: A new binuclear Cd(II)-containing ionic liquid: preparation and electrocatalytic activities. J. Org. Chem. **694** (2009) 3614–3618.
14. Das, K.; Konar, S.; Pal, P.; Jana, A.; Chatterjee, S.; Mukhopadhyay, S.: Syntheses, X-ray crystal structures and spectroscopic characterization of rare μ-di-σ pyrazole based bridging keto carbonyl complexes derived from Cd(II) salts. Polyhedron **85** (2015) 172–180.
15. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
16. BRUKER. SAINT, APEX2 and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA (2009).