



Synthesis and Crystal Structure of Bis-(μ_2 -(4-Carboxybenzyl)-methylene-4-pyridine-O,O')-dibromo-cadmium Complex

XIULI YOU* and TAO HU

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science and Technology Normal University, Nanchang 330013, P.R. China

*Corresponding author: Tel: +86 791 83805183, E-mail: xlyouzhwei@163.com

(Received: 21 November 2011;

Accepted: 12 September 2012)

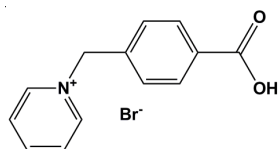
AJC-12140

Reaction of one equivalence of CdBr_2 and two equivalence of zwitter ionic carboxylate (4-carboxybenzyl)-methylene-4-pyridine ligand in water give rise to the complex $[\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_4\text{CdBr}_2]$ (I), in which the central Cd atom adopts a distorted octahedral coordination geometry that is formed from four O atoms of two bidentate (4-carboxybenzyl)-methylene-4-pyridine ligands and two Br atoms.

Key Words: Crystal structure, Cadmium complex, Zwitterionic carboxylate ligand, Pyridyl ligand.

INTRODUCTION

In the past decades, the aromatic multicarboxylate ligands have been extensively employed in the preparations of metal-organic coordination complexes¹. The resulting complexes are found to have diverse application as medicinal inorganic compounds, photosensitizer in solar cells, catalysts for organic transformations, molecular devices based on tunable properties, mimics for enzymes catalyzing redox, *etc.*². Among the large number of multicarboxylate ligands, zwitter ionic carboxylates ligand are attracted much interests due to their potential applications as redox mediators. They can undergo one-electron reduction to produce the cation radicals and play an active role as electron acceptors in charge transfer complexes in the solid state for electrical and ionic conductors³. In this work, the zwitter ionic carboxylate ligand (4-carboxybenzyl)-methylene-4-pyridine (Cbmb) is synthesized (**Scheme-I**) and is chose to react with CdBr_2 . Herein, we will report the structure of the obtained complex $[(\text{Cbmb})_2\text{CdBr}_2]$ (I).



Scheme-I: Ligand of HCbmbBr ligand

EXPERIMENTAL

All the solvents and chemicals were of analytical grade and were used without further purification. Ligand HCbmbBr was prepared according to the literature⁴.

Synthesis of complex (I): HCbmbBr (118 mg, 0.4 mmol) was dissolved in H_2O (5 mL) and the pH was adjusted to 7 with 0.1 M NaOH solution. Then, a solution of CdBr_2 (22.5 mg, 0.2 mmol) in H_2O (5 mL) was added. The resulting mixture was stirred for 0.5 h to give a clear solution and then allowed to stand for one month to produce colourless blocks. Subsequent washing with Et_2O and drying under vacuum gave $[\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_4\text{CdBr}_2]$ (I) with 63 % yield. Elemental analysis confirmed the organic content (Found: C, 44.59; H, 3.54; N, 4.42. calcd. for $\text{C}_{26}\text{H}_{22}\text{Br}_2\text{CdN}_2\text{O}_4$ (%): C, 44.66; H, 3.15; N, 4.01). IR (KBr disk): 1632 (w), 1594 (m), 1548 (w), 1507 (w), 1488 (w), 1416 (w), 1390 (w), 1374 (m), 1178 (w), 770 (m) cm^{-1} .

The elemental analyses for C, H and N were performed on a Carlo-Erba CHNO-S microanalyzer. IR spectra were recorded on a Varian 1000 FT-IR spectrometer as KBr disks (4000-400 cm^{-1}). X-ray quality single crystal of $[\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_4\text{CdBr}_2]$ was obtained directly from the above preparations. All measurements were made on a Rigaku Mercury CCD X-ray diffractometer by using graphite monochromated $\text{MoK}\alpha$ ($\lambda = 0.71070$ nm). Cell parameters were refined by using the program Crystal Clear⁵ on all observed reflections. The collected data were reduced by using the program Crystal Clear. The reflection data were also corrected for Lorentz and polarization effects. The crystal structure of complex (I) was solved by direct methods and refined on F^2 by full-matrix least-squares techniques with SHELXTL-97 program⁶. Refinement with TWIN and BASF instruction for the final positional parameters gave a value of 0.361 (13) for the Flack parameter⁷. All non-hydrogen atoms were refined isotropically. Hydrogen

atoms for the carbon atoms were placed in geometrically idealized positions and constrained to ride on their parent with $C-H = 0.97$ and 0.93 Å for methylene and aryl type H-atoms, respectively and refined in a riding mode with $U_{iso}(H) = 1.2 U_{eq}(C)$. The parameters of the crystal, data collection and refinement are given in Table-1. Crystallographic data have been deposited with the Cambridge crystallographic data centre (CCDC) (E-mail: deposit@ccdc.cam.ac.uk) as supplementary materials and the CCDC number is 853786.

TABLE-1
CRYSTAL DATA AND STRUCTURE
REFINEMENT FOR $[C_{26}H_{22}N_2O_4CdBr_2]$ (I)

Complex (I)	
Empirical formula	$C_{26}H_{22}Br_2CdN_2O_4$
Formula weight (g mol ⁻¹)	698.67
Wavelength (Å)	0.71073
Crystal system	Tetragonal,
Space group	$I4_1cd$
a (Å)	14.296 (2)
b (Å)	14.296 (2)
c (Å)	24.228 (12)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	4952 (3)
Z	8
D (Mg m ⁻³)	1.874
F(000)	2736
Absorption coefficient (mm ⁻¹)	4.146
θ Range for data collection (°)	3.3?27.5
Limiting indices	-18 ≤ h ≤ 18, -18 ≤ k ≤ 18, -31 ≤ l ≤ 31
Independent reflections	2178 [(R(int) = 0.116)]
Goodness-of-fit on F ²	1.078
Final R1 and wR ² [I > 2σ(I)]	0.0468, 0.0762
R1 and wR ² indices (all data)	0.0642, 0.0710
Largest diff. Peak and hole (e Å ⁻³)	0.67 and -0.72

RESULTS AND DISCUSSION

The structure of complex $[C_{26}H_{22}N_2O_4CdBr_2]$ and its main bond length and angles are listed in Fig. 1 and Table-2, respectively. In the structure of complex, there is a C_2 axis through the central Cd atom that is strongly coordinated by four O atoms from two carboxylate groups of two (Cbmp) ligands and two cis Br atoms, hence forming a distorted octahedral coordination geometry in which Br1 and O1i atoms are in the axial position with angle O1i-Cd1-Br1 at 142.94 (10)° and O1, O2, Br1i and O2i atoms are in the plane. Such a coordination geometry of Cd is only found in complex $[Cd\{CH_{30}(OH)C_6H_3CHN(CH_2)_2OH\}_2Br_2]$ ⁸. The coordination sphere consists two kinds of Cd-O bond lengths, one of which is weakly bonded to Cd atom [Cd-O2 = $2.282(4)$ Å and Cd-O1 = $2.629(5)$ Å]. The Cd-Br distance at 2.6368 (11) Å is similar to that in $[Cd\{CH_3O(OH)C_6H_3CHN(CH_2)_2OH\}_2Br_2]$ ($2.627(2)$ Å)⁸ and is slightly shorter than those found in complexes $[CdBr_2(C_{10}H_{12}N_2O)_2(H_2O)_2]$ ($2.6855(5)$ Å)⁹ and $[CdBr_2\{Ph_3P(CH_2)_3CO_2\}_2]$ (2.753 Å)¹⁰, in which the Cd atoms are all six-coordinated. On the other hand, the packing view of $[C_{26}H_{22}N_2O_4CdBr_2]$ are shown in Fig. 2. It can be seen along

the c axis, every molecules are crossed to each other with the metal center as the axis. The distance between two adjacent metals are $9.3692(26)$ Å.

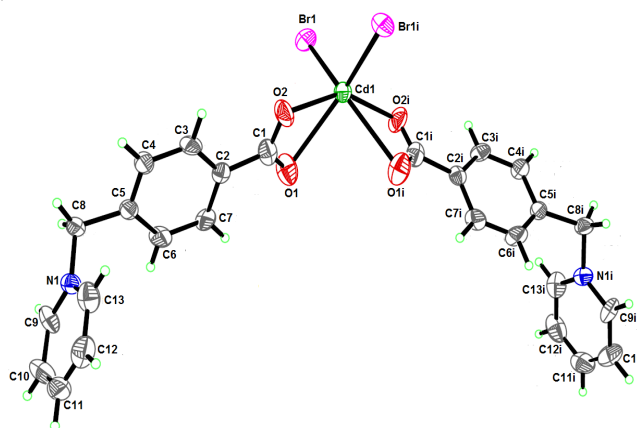


Fig. 1. Crystal structure of $[C_{26}H_{22}N_2O_4CdBr_2]$ with 50 % thermal ellipsoids. Symmetry transformation was used to generate equivalent atoms: symmetry codes: (i) $-x + 1, -y, z$

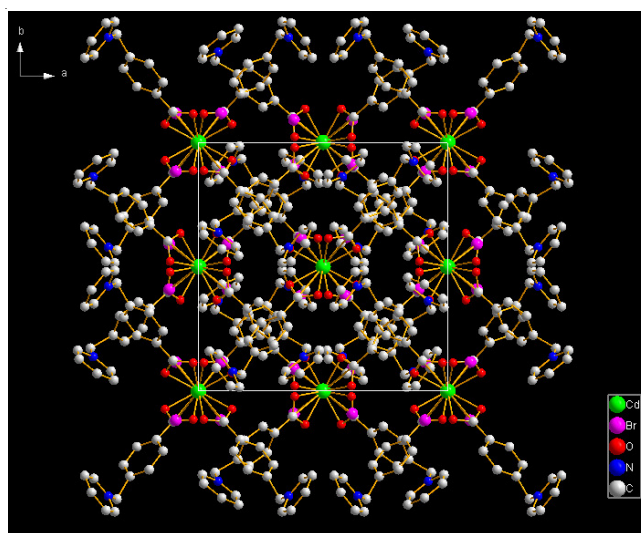


Fig. 2. Packing view of $[C_{26}H_{22}N_2O_4CdBr_2]$ extending along the c axis

TABLE-2
SELECTED BOND LENGTHS (Å) AND
ANGLES (°) FOR $[C_{26}H_{22}N_2O_4CdBr_2]$

Cd1—O2	2.282 (4)	Cd1—O2 ⁱ	2.282 (4)
Cd1—O1	2.629 (5)	Cd1—O1 ⁱ	2.629 (5)
Cd1—Br1	2.6368 (10)	Cd1—Br1 ⁱ	2.6368 (10)
Cd1—C1 ⁱ	2.800 (7)	Cd1—C1	2.800 (7)
O1—C1	1.232 (8)	O2—C1	1.279 (8)
N1—C8	1.500 (7)		
O2—Cd1—O2 ⁱ	147.1 (2)	O2—Cd1—O1	52.66 (15)
O2 ⁱ —Cd1—O1	99.65 (15)	O2—Cd1—O1 ⁱ	99.65 (15)
O2 ⁱ —Cd1—O1 ⁱ	52.66 (15)	O1—Cd1—O1 ⁱ	78.3 (2)
O2—Cd1—Br1	106.72 (12)	O2 ⁱ —Cd1—Br1	92.89 (12)
O1—Cd1—Br1	97.33 (11)	O1 ⁱ —Cd1—Br1	142.94 (10)
O2—Cd1—Br1 ⁱ	92.89 (12)	O2 ⁱ —Cd1—Br1 ⁱ	106.72 (12)
O1—Cd1—Br1 ⁱ	142.94 (10)	O1 ⁱ —Cd1—Br1 ⁱ	97.33 (11)
Br1—Cd1—Br1 ⁱ	106.70 (5)		

Symmetry codes: (i) $-x + 1, -y + 0, z + 0$

ACKNOWLEDGEMENTS

The authors are grateful for the financial support by Jiangxi Science and Technology Normal University, P.R. China.

REFERENCES

1. O.M. Yaghi, H.L. Li, C. Davis, D. Richardson and T.L. Groy, *Acc. Chem. Res.*, **31**, 474 (1998).
2. L. Carlucci, G. Ciani and D.M. Proserpio, *Coord. Chem. Rev.*, **246**, 247 (2003).
3. Q.X. Yao, Z.F. Ju and J. Zhang, *Inorg. Chem.*, **48**, 1266 (2009).
4. Y.Q. Sun, J. Zhang, Z.F. Ju and G.Y. Yang, *Cryst. Growth Des.*, **5**, 1939 (2005).
5. Rigaku, Crystal Clear and Crystal Structure. Rigaku Corporation, Tokyo, Japan (2001).
6. G.M. Sheldrick, SHELXS-97 and SHELXL-97, Program for the X-ray Crystal Structure Solution, University of Göttingen, Germany (1997).
7. H.D. Flack, *Acta Cryst.*, **A39**, 876 (1983).
8. W. Hu, Y.F. Zhao, X.L. Zhao, X. i and X.G. Cui, *Chin. J. Struct. Chem.*, **20**, 134 (2001).
9. H.Z. Dong, Z.L. Chu and N.L. Hu, *Acta Cryst.*, **E65**, m358 (2009).
10. S.L. Li and T.C.W. Mak, *Polyhedron*, **16**, 199 (1997).