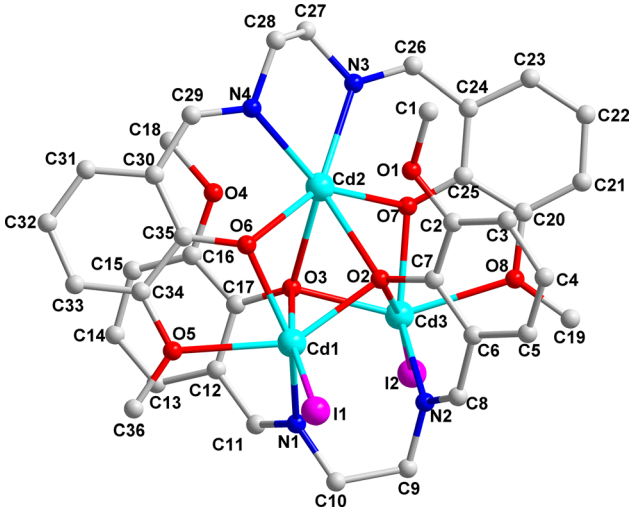
Jin Hu and Xin-Hua Lu*

Crystal structure of diiodido-bis(6,6′-dimethoxy-2,2′-(ethane-1,2-diylbis(nitrilomethanylylidene)) diphenolato)tricadmium(II), $C_{36}H_{36}Cd_3I_2N_4O_8$



https://doi.org/10.1515/ncrs-2022-0313
Received June 18, 2022; accepted July 22, 2022;
published online August 29, 2022

Abstract

$C_{36}H_{36}Cd_3I_2N_4O_8$, orthorhombic, *Pbca* (no. 61), a = 18.909(4) Å, b = 16.149(3) Å, c = 26.050(5) Å, V = 7955(3) Å^3, Z = 8, $R_{gt}(F)$ = 0.0439, $wR_{ref}(F^2)$ = 0.0752, T = 293(2) K.

CCDC no.: 2192002

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The reagents used were purchased from commercial sources without further purification. A methanol (4 mL) solution of 6,6′-dimethoxy-2,2′-(ethane-1,2-diylbis(nitrilomethanylylidene))diphenol (H_2dedp, 0.02 mmol) was added dropwise into a methanol solution (4 mL) of CdI_2 (0.03 mmol). A clear solution was obtained after filtration and placed in a closed container at room temperature. Light yellow crystals can be obtained after four weeks (yield 47%, based H_2dedp).

Table 1: Data collection and handling.

Crystal:	Yellow prism
Size:	0.18 × 0.16 × 0.13 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	3.20 mm^{-1}
Diffractometer, scan mode:	Bruker D8 VENTURE PHOTON, φ and ω
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	79820, 7401, 0.048
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 7234
$N(param)_{refined}$:	478
Programs:	SHELX [1], Bruker [2, 3]

Experimental details

Hydrogen atoms on C19 and C36 were located in a difference Fourier map and C–H distances were constrained to 0.96 Å. Hydrogen atoms on other carbon were positioned geometrically and refined as riding atoms, with C–H = 0.97 (CH_2), 0.96 Å (CH_3), 0.93 Å (aromatic, CH). Hydrogen atoms were refined with U_{iso}(H) = 1.2 U_{eq}(C).

Comment

Schiff-bases have been proven to be excellent building blocks for assembling new complexes since they contain N-atom and O-atom donors and can coordinate to almost all metal ions with various coordination modes [4, 5]. So far, a lot of complexes based on 6,6′-dimethoxy-2,2′-(ethane-1,2-diylbis(nitrilomethanylylidene)) diphenol (H_2dedp) have been synthesized and characterized, such as Cu(II), Zn(II), Pb(II), Fe(III), Co(III) and Mn(III) complexes [6–12]. In order to further enrich the numbers of

***Corresponding author: Xin-Hua Lu**, School of Chemical and Material Engineering, Nanjing Polytechnic Institute, 210048, Nanjing, China, E-mail: xinhualu@njpi.edu.cn. https://orcid.org/0000-0003-4831-7456
Jin Hu, School of Chemical and Material Engineering, Nanjing Polytechnic Institute, 210048, Nanjing, China, E-mail: hujin@njpi.edu.cn

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

Atom	x	y	z	U_{iso}*/U_{eq}
Cd1	0.06034 (2)	0.90745 (2)	0.34356 (2)	0.03574 (10)
Cd2	0.14317 (2)	0.71908 (2)	0.32778 (2)	0.03878 (11)
Cd3	−0.01573 (2)	0.72699 (2)	0.38969 (2)	0.03633 (10)
I1	0.08519 (2)	1.04983 (2)	0.39713 (2)	0.05638 (12)
I2	−0.14931 (2)	0.66610 (2)	0.38062 (2)	0.04845 (11)
N1	−0.0619 (2)	0.9028 (3)	0.34126 (17)	0.0402 (10)
N2	−0.0377 (2)	0.8467 (3)	0.43753 (16)	0.0387 (10)
N3	0.1962 (3)	0.5858 (3)	0.32795 (18)	0.0519 (13)
N4	0.2424 (2)	0.7225 (3)	0.27530 (16)	0.0445 (11)
O1	0.2221 (2)	0.7508 (3)	0.41517 (15)	0.0554 (11)
O2	0.09403 (18)	0.8018 (2)	0.39510 (12)	0.0357 (8)
O3	0.02452 (18)	0.7668 (2)	0.30980 (12)	0.0373 (8)
O4	0.0796 (2)	0.6923 (2)	0.22936 (14)	0.0464 (10)
O5	0.0655 (2)	0.9718 (2)	0.25822 (14)	0.0481 (10)
O6	0.15058 (18)	0.8581 (2)	0.29815 (13)	0.0394 (8)
O7	0.07047 (19)	0.6340 (2)	0.37877 (13)	0.0418 (9)
O8	0.0089 (2)	0.6497 (3)	0.46996 (14)	0.0532 (10)
C1	0.2908 (4)	0.7222 (6)	0.4257 (3)	0.107 (3)
H1A	0.311468	0.700247	0.394908	0.128*
H1B	0.319222	0.767209	0.438113	0.128*
H1C	0.288729	0.679495	0.451332	0.128*
C2	0.1854 (3)	0.7842 (4)	0.4559 (2)	0.0464 (14)
C3	0.2121 (3)	0.7933 (5)	0.5048 (2)	0.0657 (19)
H3A	0.257788	0.775927	0.512584	0.079*
C4	0.1696 (4)	0.8289 (5)	0.5424 (2)	0.074 (2)
H4A	0.187144	0.835194	0.575477	0.088*
C5	0.1026 (3)	0.8546 (4)	0.5314 (2)	0.0604 (18)
H5A	0.075282	0.879144	0.556922	0.072*
C6	0.0746 (3)	0.8444 (4)	0.4821 (2)	0.0433 (13)
C7	0.1165 (3)	0.8097 (3)	0.44321 (19)	0.0378 (12)
C8	0.0030 (3)	0.8733 (3)	0.4730 (2)	0.0410 (13)
H8A	−0.014508	0.914312	0.494574	0.049*
C9	−0.1057 (3)	0.8890 (3)	0.4297 (2)	0.0441 (13)
H9A	−0.116980	0.922204	0.459618	0.053*
H9B	−0.142925	0.848375	0.425136	0.053*
C10	−0.1015 (3)	0.9446 (3)	0.3823 (2)	0.0466 (14)
H10A	−0.148810	0.957420	0.370414	0.056*
H10B	−0.078165	0.996120	0.391175	0.056*
C11	−0.0949 (3)	0.8798 (3)	0.3006 (2)	0.0462 (14)
H11A	−0.142611	0.893299	0.298038	0.055*
C12	−0.0636 (3)	0.8344 (3)	0.2582 (2)	0.0438 (13)
C13	−0.0930 (4)	0.8459 (4)	0.2092 (2)	0.0599 (17)
H13A	−0.132707	0.879321	0.205361	0.072*
C14	−0.0642 (4)	0.8087 (5)	0.1672 (3)	0.070 (2)
H14A	−0.083516	0.817684	0.134815	0.084*
C15	−0.0060 (4)	0.7575 (4)	0.1727 (2)	0.0564 (17)
H15A	0.014067	0.732854	0.143958	0.068*
C16	0.0223 (3)	0.7428 (3)	0.22044 (19)	0.0402 (13)
C17	−0.0055 (3)	0.7807 (3)	0.26475 (18)	0.0359 (12)
C18	0.1111 (4)	0.6547 (5)	0.1851 (2)	0.070 (2)
H18A	0.150406	0.621026	0.195496	0.084*
H18B	0.076681	0.620794	0.167969	0.084*
H18C	0.127328	0.697049	0.162032	0.084*
C19	−0.0208 (4)	0.6650 (4)	0.5189 (2)	0.074 (2)
H19A	−0.037377	0.612812	0.531707	0.088*
H19B	0.013313	0.679892	0.544607	0.088*
H19C	−0.065317	0.693482	0.517837	0.088*
C20	0.0654 (3)	0.5961 (3)	0.4671 (2)	0.0451 (13)
C21	0.0906 (4)	0.5505 (4)	0.5073 (2)	0.0636 (18)
H21A	0.068493	0.553918	0.539089	0.076*
C22	0.1488 (4)	0.4992 (5)	0.5011 (3)	0.074 (2)
H22A	0.165526	0.468097	0.528544	0.088*
C23	0.1813 (4)	0.4946 (4)	0.4546 (3)	0.0674 (19)
H23A	0.220521	0.460395	0.450759	0.081*
C24	0.1570 (3)	0.5406 (3)	0.4124 (2)	0.0473 (14)
C25	0.0973 (3)	0.5916 (3)	0.4171 (2)	0.0418 (13)
C26	0.1988 (3)	0.5361 (4)	0.3663 (2)	0.0526 (16)
H26A	0.230963	0.492646	0.364061	0.063*
C27	0.2496 (4)	0.5740 (4)	0.2873 (2)	0.0634 (19)
H27A	0.226461	0.560684	0.255145	0.076*
H27B	0.280750	0.528550	0.296314	0.076*
C28	0.2917 (3)	0.6526 (4)	0.2817 (2)	0.0563 (17)
H28A	0.320719	0.661229	0.311916	0.068*
H28B	0.322529	0.648718	0.252060	0.068*
C29	0.2493 (3)	0.7658 (3)	0.2346 (2)	0.0438 (13)
H29A	0.287307	0.752072	0.213571	0.053*
C30	0.2056 (3)	0.8333 (3)	0.21721 (19)	0.0389 (12)
C31	0.2103 (3)	0.8549 (4)	0.1649 (2)	0.0554 (16)
H31A	0.243545	0.828374	0.144351	0.067*
C32	0.1679 (4)	0.9131 (4)	0.1439 (2)	0.0666 (19)
H32A	0.172001	0.926131	0.109259	0.080*
C33	0.1185 (4)	0.9531 (4)	0.1741 (2)	0.0550 (16)
H33A	0.088816	0.992541	0.159551	0.066*
C34	0.1130 (3)	0.9349 (3)	0.2252 (2)	0.0398 (12)
C35	0.1565 (3)	0.8741 (3)	0.24888 (19)	0.0351 (12)
C36	0.0208 (4)	1.0358 (4)	0.2383 (3)	0.072 (2)
H36A	−0.005419	1.013547	0.209940	0.086*
H36B	0.057471	1.075746	0.232340	0.086*
H36C	−0.011899	1.047167	0.265640	0.086*

complexes based on this ligand, we selected H_2dedp as ligand to react with CdI_2 and obtained a new complex $[Cd_3(dedp)_2I_2]$.

The asymmetrical unit of the title structure contains three Cd(II) ions, two 6,6′-dimethoxy-2,2′-(ethane-1,2-diylbis (nitrilomethanylylidene))diphenolato anions (dedp^{2-}) and two iodine anions. The coordination sites of Cd1 are occupied by four oxygen atoms (O2, O3, O5, O6) and one nitrogen atom (N1) from two dedp^{2-} ligands, and by one iodine atom (I1), resulting in a distorted octahedral CdO_4NI coordination environment. The Cd1–O bond lengths are 2.224(3), 2.262(3), 2.456(4) and 2.527(3) Å, respectively; the Cd1–N bond length is 2.313(4) Å and the Cd1–I bond length is 2.7304(7) Å; these values are comparable to the bond lengths reported in the literature for comparable Cd(II) complexes [13, 14]. Cd2 is six-coordinated by four oxygen atoms (O2, O3, O6, O7) and two

nitrogen atoms (N3 and N4) from two $dedp^{2-}$ ligands, leading to a distorted octahedral CdO_4N_2 coordination environment. The Cd2–O bond lengths of 2.354(4), 2.379(3), 2.393(3), 2.418(3) Å and the Cd2–N bond lengths of 2.322(4) and 2.375(5) Å are close to those of Cd1–O and Cd1–N. Cd3 ion is also six-coordinated and located in a distorted octahedral CdO_4NI coordination environment formed by four oxygen atoms (O2, O3, O7, O8) and one nitrogen atom (N2) from two $dedp^{2-}$ ligands, and by one iodine atom (I2). The Cd3–O bond lengths are 2.234(3), 2.307(3), 2.406(3), 2.479(4) Å, the Cd3–N bond length is 2.338(4) Å, and the Cd3–I bond length is 2.7208(7) Å; these values are within the normal ranges and close to those reported in other Cd(II) complexes [13, 14]. Two phenolate oxygen atoms (O2, O3) behave as μ_3–O coordinating with three Cd(II) ions, while the other two phenolate oxygen atoms (O6, O7) act as μ_2–O bridging two Cd(II) ions. As a result, Cd(II) ions are liked by the phenolate oxygen atoms leading to a trinuclear Cd(II) complex. The Cd1–Cd2, Cd1–Cd3 and the Cd2–Cd3 distances are 3.4461(8), 3.4650(7) and 3.4124(8) Å, respectively. In the crystal, adjacent molecules are packed through van der Waals forces resulting in a three-dimensional supramolecular architecture.

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.
Research funding: None declared.
Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
2. Bruker. *SADABS*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2000.
3. Bruker. *APEX3 and SAINT*; Bruker AXS Inc.: Madison, Wisconsin, USA, 2016.
4. Zoubi W. A., Al-Hamdani A. A. S., Kaseem M. Synthesis and antioxidant activities of Schiff bases and their complexes: a review. *Appl. Organomet. Chem.* 2016, *30*, 810–817.
5. Polt R., Kelly B. D., Dangel B. D., Tadikonda U. B., Ross R. E., Raitsimring A. M., Astashkin A. V. Optically active 4- and 5-coordinate transition metal complexes of bifurcated dipeptide Schiff bases. *Inorg. Chem.* 2003, *42*, 566–574.
6. Zhang S.-L., Fan X.-F., Du R.-L., Shen B.-W., Song X.-D., Wei X.-Q., Li S.-S. Synthesis, crystal structures and magnetism of $Cu^{II}Ln^{III}$ N_2O_4-donor coordination compounds involving dicyanamides. *Polyhedron* 2021, *206*, 115336.
7. Majumdar D., Das S., Thomas R., Ullah Z., Sreejith S. S., Das D., Shukla P., Bankura K., Mishra D. Syntheses, X-ray crystal structures of two new Zn(II)-dicyanamide complexes derived from H_2vanen-type compartmental ligands: investigation of thermal, photoluminescence, in vitro cytotoxic effect and DFT-TDDFT studies. *Inorg. Chim. Acta* 2019, *492*, 221–234.
8. Parr J., Ross A. T., Slawin A. M. Z. Tricoordinate complexes of lead(ll) with innocent Schiff base ligands. *Polyhedron* 1997, *16*, 2765–2770.
9. Provis-Evans C. B., Lau S., Krewald V., Webster R. L. Regioselective alkyne cyclotrimerization with an in situ-generated [Fe(II)H(salen)] · Bpin catalyst. *ACS Catal.* 2020, *10*, 10157–10168.
10. Ghosh M. K., Pathak S., Ghorai T. K. Synthesis of two mononuclear Schiff base metal (M = Fe, Cu) complexes: MOF structure, dye degradation, H_2O_2 sensing, and DNA binding property. *ACS Omega* 2019, *4*, 16068–16079.
11. Assey G., Butcher R. J., Gultneh Y. Acetato(aqua){6,6′- dimethoxy-2,2′-[ethane-1,2-diylbis(nitrilomethanylyl-idene)] diphenolato} cobalt(III) methanol disolvate. *Acta Crystallogr.* 2012, *E68*, m962–m963.
12. Gutierrez A., Perpinan M. F., Sanchez A. E., Torralba M. C., Gonzalez V. Water inclusion mediated structural diversity and the role of H-bonds in molecular assemblies of manganese(III) bicompartmental Schiff-base complexes. *Inorg. Chim. Acta* 2016, *453*, 169–178.
13. Meng X.-R., Wu X.-J., Li D.-W., Hou H.-W., Fan Y.-T. Influence of the anion on the coordination mode of an unsymmetrical N-heterocyclic ligand in Cd(II) complexes: from discrete molecule to one- and two-dimensional structures. *Polyhedron* 2010, *29*, 2169–2628.
14. Liu Y.-J., Cheng D., Li Y.-X., Zhang J.-D., Yang H.-X. A new one-dimensional Cd^{II} coordination polymer incorporating 2,2′-(1,2-phenylene)bis(1*H*-imidazole-4,5-dicarboxylate). *Acta Crystallogr.* 2018, *C74*, 1128–1132.