

Two New Iodo-Bridged Cadmium(II) Polymers with 1,4-dioxane and Ethanolamine Ligands: Synthesis and Crystal Structures

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Abstract: Two new organic/inorganic composite coordination polymers have been synthesised by the reaction of cadmium (II) iodide with 1,4-dioxane, $[\text{CdI}_2(\text{C}_4\text{H}_8\text{O}_2)]_n$ (1) and with N-(2,4-dichlorobenzylidene)ethanolamine, $[\text{Cd}_2\text{I}_4(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_2]_n$ (2). These complexes have been structurally characterised by X-ray diffraction analysis. Complex 1 crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.2028(3)$, $b = 14.3556(5)$, $c = 7.6594(3)$ Å, $\beta = 100.513(1)^\circ$, $V = 886.80(6)$ Å³ and $Z = 4$. Complex 2 crystallizes in the orthorhombic space group $Pccn$ with $a = 8.7369(6)$, $b = 13.2514(9)$, $c = 14.3794(11)$ Å, $V = 1664.8(2)$ Å³ and $Z = 8$. The crystal structure analysis shows an octahedral environment around the cadmium atom in complex 1 and the crystal packing comprises of doubly iodo-bridged polymeric layers, where the two independent 1,4 dioxane ligands act as are bridging species through O atoms. The structure of 2 is an iodo bridged one-dimensional chain with the two independent Cd(II) ions alternating along the polymer. Here one Cd(II) ion is coordinated in a slightly distorted octahedral geometry by two chelating ethanolamine ligands via O, N donors and two iodo ligands. The other Cd(II) ion is tetrahedrally coordinated by four iodo ligands.

Keywords: Cadmium (II), Crystal Structure, Tetrahedral and Octahedral Coordination

1. Introduction

Organometallic supramolecular chemistry is an increasingly active discipline, which represents an extensive expansion of many research areas, including chemical, pharmaceutical, biological and material sciences. The supramolecular recognition field attracts increasingly special attention [1-3], and cadmium iodide complexes have received special attention particularly in the view of their remarkable structural diversity. To the best of our knowledge, there are only a few structurally known examples among the family of inorganic/organic supramolecular [4-9]. The Dakar group

have previously synthesized and characterised a Cd complex with the Schiff base N, N'-bis(4-methoxybenzylidene)ethylenediamine [10]. On continuation of our interest in Cd derivatives, the present study focusses on the synthesis and characterization of cadmium iodide complexes with 1,4 dioxane and ethanolamine ligands (Figure 1). The two new complexes were characterized by single crystal X-ray diffraction.

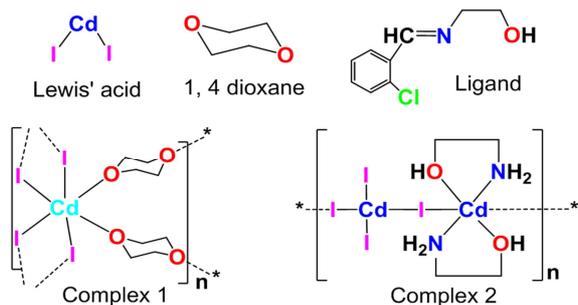


Figure 1. Representations of reagents and compounds related to this study.

2. Experimental

2.1. Materials and Physical Measurements

All reagents (1,4-dioxane, ethanolamine, 2,4-dichlorobenzaldehyde and cadmium iodide 98%) were purchased from Aldrich and were used without further purification. The solvent use for the synthesis is ethanol absolute. The complexes have been structurally characterized by single crystal X-ray diffraction.

2.2. Synthesis

2.2.1. Synthesis of Complex 1

The synthesis of compound of the complex 1 was performed as following: (5 mmol, 1.8311 g) of cadmium iodide was completely dissolved in 20 mL methanol. Then 0,5 mL of 1,4-dioxane (5 mmol) was added to the solution which was stirred for about 1h. The resulting solution was left for slow evaporation of at room temperature, leading to grey crystals suitable for single crystal X-ray diffraction.

2.2.2. Synthesis of Complex 2

The cadmium complex 2 was synthesized by mixing 2,136 g (5 mmol) of N-(2,4-dichlorobenzylidene)ethanolamine, obtained by condensing 2,4 dichlorobenzaldehyde with ethanolamine, and 1.811 g, (5 mmol) cadmium iodide in ethanol. This mixture was refluxed for 2h at a temperature of 80°C. The obtained clear yellow solution was filtered and evaporated slowly for a few days to give yellow crystals. After characterization, it was observed that the ligand underwent hydrolysis to form ethanolamine that reacted with CdI_2 to give complex 2 and associated release of a dichlorobenzaldehyde molecule (Figure 2).

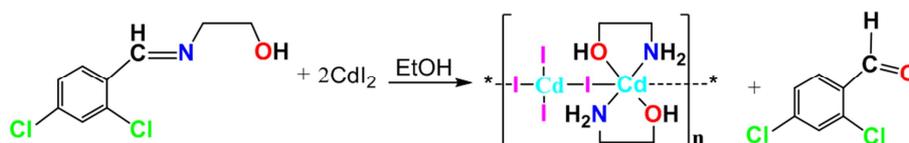


Figure 2. Synthesis of complex $[\text{Cd}_4(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_2]$ (2).

2.3. X-Ray Diffraction Analyses

Reflections were measured on a Bruker D8 Quest diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073\text{\AA}$). Software package used for the intensity integration was Saint (v8.40a) [11] and absorption correction was performed with SADABS. [12] The structures were solved with direct methods using SHELXT-2014/5. [3] Least-squares refinement was performed with SHELXL-2018/3 [13] against $|F_h^o|^2$ of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were placed on calculated

positions or located in difference Fourier maps. All calculated hydrogen atoms were refined with a riding model [14]. The structures obtain were draw by the application Olex2 [15]. Crystal data and details of structure refinement for the two complexes are summarized in Table 1.

Accession codes:

CCDC 2165544 (1) and 2165540 (2) contain the supplementary crystallographic data for this paper. Copies can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (fax: int. Code +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Table 1. Crystallographic data for complexes 1 and 2.

Compound	1	2
Empirical formula	$\text{C}_4\text{H}_8\text{CdI}_2\text{O}_2$	$\text{C}_2\text{H}_7\text{CdI}_2\text{NO}$
Formula weight (g/mol)	454.30	427.29
Crystal system	Monoclinic	Orthorhombic
Space group	$P 2_1/c$	$P ccn$
Crystal size mm	$0.23 \times 0.20 \times 0.14$	$0.17 \times 0.14 \times 0.09$
$a/\text{\AA}$	8.2028 (3)	8.7369 (6)
$b/\text{\AA}$	14.3556 (5)	13.2514 (9)
$c/\text{\AA}$	7.6594 (3)	14.3794 (11)
$\alpha/^\circ$	90	90
$\beta/^\circ$	100.513 (1)	90
$\gamma/^\circ$	90	90
Volume/ \AA^3	886.80 (6)	1664.8 (2)
Z	4	8
$D_x, \text{g/cm}^3$	3.403	3.410
μ/mm^{-1}	9.362	9.957

Compound	1	2
F(000)	808	1504
2 θ range for data collection/ $^{\circ}$	2.52 - 33.19	2.79 - 33.17
Index ranges	-12 $\leq h \leq$ 12, -22 $\leq k \leq$ 21, -11 $\leq l \leq$ 11	-13 $\leq h \leq$ 13, -20 $\leq k \leq$ 20, -22 $\leq l \leq$ 14
Reflections collected	15454	17824
Independent reflections	3354 [$R_{int} = 0.0241$]	3053 [$R_{int} = 0.0494$]
Parameters	83	71
Final R indexes [$I \geq 2\sigma(I)$]	R1 = 0.0167 wR2 = 0.0354	R1 = 0.0688 wR2 = 0.1278
Residuals / e \AA^{-3}	0.891 / -0.913	2.391 / -1.917

3. Results and Discussion

A perspective view of the molecular structure of complex 1, $[\text{CdI}_2(\text{C}_4\text{H}_8\text{O}_2)]_n$, is illustrated in Figure 3 together with a selection of bond lengths and angles. The cadmium atom is octahedrally surrounded by four bridged iodine atoms and two *cis* located 1,4 dioxane molecules, giving rise to a layer developed in the *bc*-plane. The Cd-I bond lengths fall in a range between 2.8748(2) and 2.9363(2) \AA , while the two bidentate 1,4 dioxane present Cd-O bond distances of 2.3992 (13) and 2.4468 (13) \AA .

The crystal structure of complex 1 consists of an infinite 2D-dimensional architecture built by iodo- and dioxane-bridging molecules, as displayed in Figure 4. The Cd-I1-Cd and Cd-I2-Cd bridging angles are comparable of 90.016(5) and 91.181(5) $^{\circ}$ respectively. This arrangement is due to the dioxane connecting behaviour and differs from the parent compound $[\text{CdCl}_2(\text{NC}_3\text{H}_4\text{CH}_2\text{NH}_2)]_n$ [5], where a doubly chloro-bridged polymeric chain was detected.

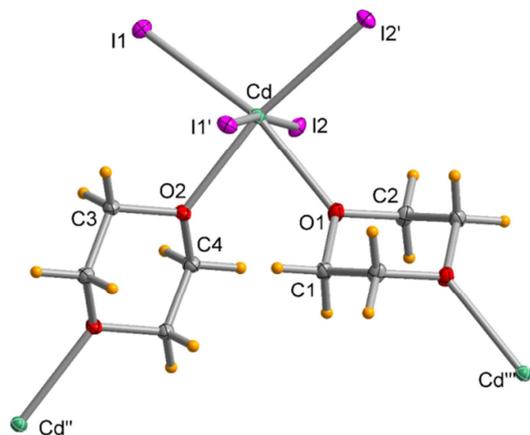


Figure 3. An ORTEP drawing (ellipsoid at 50% probability) of the molecular structure of complex 1 with the atom numbering scheme.

Selected bond lengths and angles (\AA , deg): Cd(1)-I(1) 2.93132(18), Cd(1)-I(2) 2.93379(18), Cd(1)-I(1)' 2.93629(18), Cd(1)-I(2)' 2.87480(17), Cd(1)-O(1) 2.4468(13), Cd(1)-O(2) 2.3992(13), O(2)-Cd(1)-O(1) 76.65(5), O(1)-Cd(1)-I(1) 163.08(3), O(1)-Cd(1)-I(2) 84.04(3), O(1)-Cd(1)-I(1)' 88.06(3), O(1)-Cd(1)-I(2)' 91.96(3), O(2)-Cd(1)-I(1) 88.37(3), O(2)-Cd(1)-I(2) 91.49(3), O(2)-Cd(1)-I(1)' 84.74(3), O(2)-Cd(1)-I(2)' 167.42(3), I(1)-Cd(1)-I(2) 88.591(5), I(1)-Cd(1)-I(2)' 103.608(6), I(2)-Cd(1)-I(2)' 92.613(6), I(2)'-Cd(1)-I(1)'

89.629(5). Symmetry codes ($'$): $x, -y+3/2, z-1/2$; ($''$) $1-x, 1-y, 1-z$; ($'''$) $-x, 1-y, -z$.

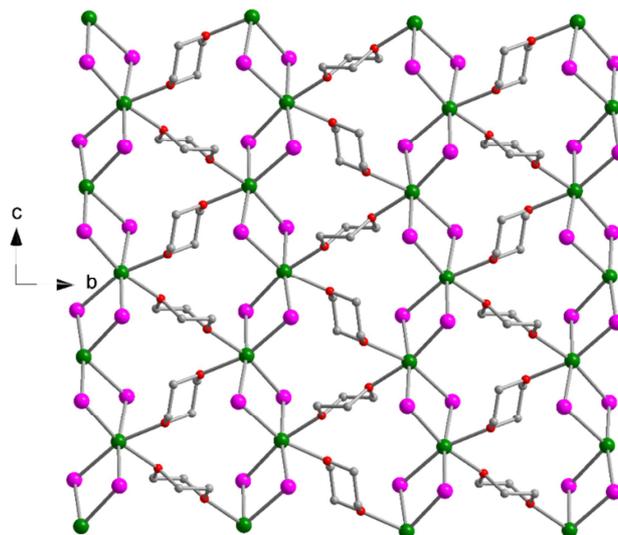


Figure 4. 2D supramolecular architecture of compound 1. Hydrogen atoms are omitted for clarity.

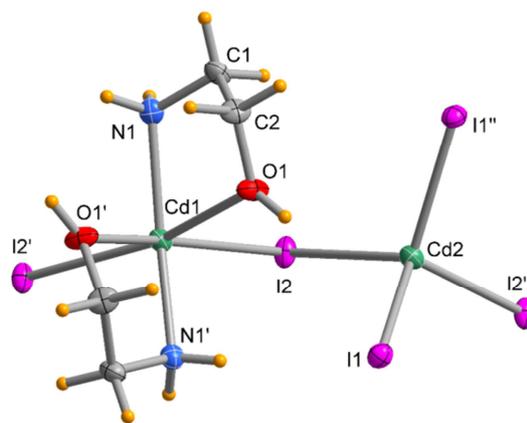


Figure 5. The molecular structure (ORTEP drawing with ellipsoid probability at 50%) of complex 2 with indication of coordination geometry of Cd atoms.

The crystallographic structural results of $[\text{CdI}_4(\text{NH}_2\text{CH}_2\text{CH}_2\text{OH})_2]_n$ (2) evidenced two independent Cd(II) ions in the asymmetric unit (Figure 5). One Cd(II) ion is located on a 2-fold axis and is coordinated in a slightly distorted octahedral coordination environment by two symmetry related N, O chelating ethanolamine ligands and two *cis* located iodide ligands. The second Cd(II) ion

possesses a C₂ symmetry and is coordinated by four iodide ligands in a slightly distorted tetrahedral geometry (Figure 5). The Cd(NH₂CH₂CH₂OH)₂ units are connected to the CdI₄ moieties *via* bridging iodide ligands I2 to form a one-dimensional polymer along [100] direction (Figure 6). The crystal structure is very similar to that of [Cd₂I₄(cyclohexane-1,2-diamine)] reported by Cui *et al.* [4] However in the latter case the bridging iodide ligands.

Selected bond lengths and angles (Å, °): Cd(1)-I(2)

2.9212(9), Cd(1)-N(1) 2.267(8), Cd(1)-O(1) 2.459(7), Cd(2)-I(1) 2.7536(9), Cd(2)-I(2) 2.8363(10), N(1)-Cd(1)-N(1)' 156.9(4), O(1)-Cd(1)-I(2)' 165.46(19), I(2)'⁻-Cd(1)-I(2) 103.59(4), N(1)-Cd(1)-O(1) 73.2(3), N(1)-Cd(1)-O(1)' 88.8(3), N(1)-Cd(1)-I(2)' 98.7(2), O(1)-Cd(1)-I(2) 89.42(19), O(1)-Cd(1)-O(1)' 78.5(4), N(1)-Cd(1)-I(2) 95.5(2), I(1)-Cd(2)-I(2) 110.279(18), I(1)-Cd(2)-I(1)'' 110.60(5), I(1)-Cd(2)-I(2)'' 113.429(18), I(2)''⁻-Cd(2)-I(2) 98.36(4). Symmetry codes ('') -x+1/2, -y+1/2, z; ('') -x+3/2, -y+1/2, z.

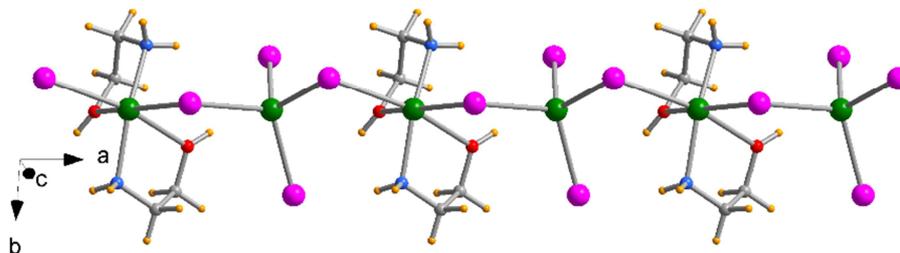


Figure 6. The one-dimensional structure of complex 2 elongated in the direction of axis a.

In the crystal, iodine I1 atoms play a key role to act as acceptor of H-bonds with OH and NH₂ groups (Table 2), thus connecting the zig-zag chains in a two-dimensional framework (Figure 7).

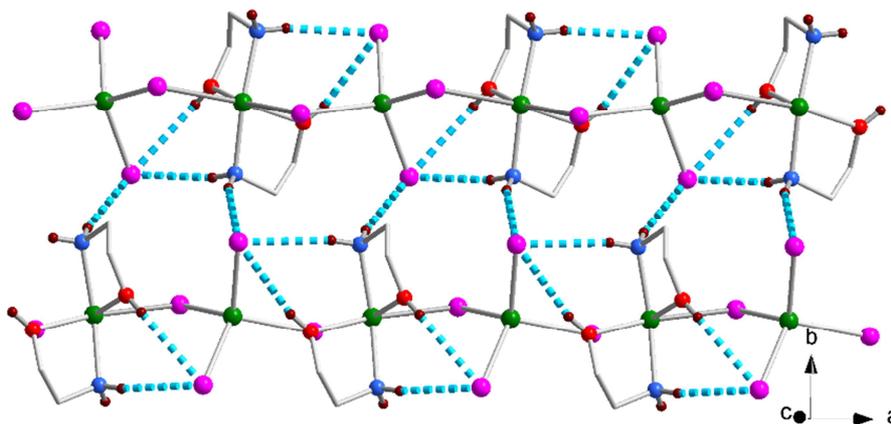


Figure 7. Crystal packing showing the OH...I and NH...I hydrogen bonds (dashed lines). Only H atoms of OH and NH₂ shown for clarity.

Table 2. Hydrogen-bond parameters (Å, °) for complex 2.

D-H	A	D-H	H...A	D...A	D-H...A	Symmetry codes
O1-H1O	I1	0.85 (11)	2.94 (11)	3.658 (7)	143 (11)	-
N1-H1A	I1	0.91	2.85	3.720 (8)	160	1-x, 1/2+y, 1/2-z
N1-H1B	I1	0.91	2.84	3.729 (7)	166	1/2-x, 1/2-y, z

4. Conclusions

Two novel cadmium iodide complexes with 1,4-dioxane (1) and ethanolamine (2) ligands have been successfully synthesized and characterized by single crystal X-ray diffraction. Within the two polymeric organic/inorganic complexes built by bridging iodide the metals display a distorted octahedral coordination environment in 1 or octahedral/tetrahedral in 2. The latter structure reveals a rich supramolecular architecture realized by intermolecular hydrogen-bonding interactions.

Author Contributions

We declare that this work was done by the authors named in this article and all liabilities pertaining to claims relating to the content of this article will be borne by the authors. In addition, a declaration of the role of each author is provided. Mr. Aboubacar Diop assembled the whole manuscript and wrote the initial draft, Dr. Tidiane Diop and Mouhamadou Abdoulaye Diallo conceived and supervised the study; Dr Paul Tinnemans analyse the crystal by X-ray diffraction and edited the work. Prof. Abdoul khadir Diop designed, supervised and edited the work. All the authors have accepted

responsibility for the entire content of the submitted manuscript and approved submission.

Conflict of Interest Statement

The authors declare no conflict of interests.

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References

- [1] Jian F. F., Zhao P. S., Wang Q. X., Li Y. *Inorg. Chim. Acta* 2006, 359, 5, 1473-1477.
- [2] Bogachev N. A., Starova G. L., Razzhivin A. V., Skripkin M. Y., Nikolskii A. B. *Russ. J. Gen. Chem.* 2018, 88, 1-6.
- [3] Zhang L., Wang J., Han F., Mo S., Long F., Gao Y. *J. Mol. Struct.*, 2018, 1156, 450-456.
- [4] Cui S. F., Wen Q. M., Zhou C. H. *Acta Crystallogr.* 2012, E68, m889.
- [5] Karmakar R., Choudhury C. R., Hughes D. L., Mitra S. *Inorg. Chim. Acta* 2007, 360, 2631-2637.
- [6] Pryma O. V., Petrusenko S. R., Kozozay V. N., Shishkin O. V., Zhigalko M. V., Linert W., *Z. Naturforsch.* 2003, 58b, 1117-1123.
- [7] Dobrzycki L., Woźniak K. *J. Mol. Struct.*, 2009, 921, 18-33.
- [8] Hakimi M., Mardani Z., Moeini K., Fernandes M. A. *J. Coord. Chem.*, 2012, 65, 2221-2233.
- [9] Ciurtin D. M., Smith M. D., Loye H. C. *Polyhedron*, 2003, 22, 3043-3049.
- [10] Ndiolene A., Diop T., Boye M. S., Maris T., Diassé-Sarr A. *Am. J. Heterocycl. Chem.* 2020, 6, 30-35.
- [11] SAINT V8.38A. Bruker AXS Inc., Madison, Wisconsin, USA.
- [12] Krause L., Herbst-Irmer R., Sheldrick G. M., Stalke D. *J. Appl. Cryst.*, 2015, 48, 3-10.
- [13] Sheldrick G. M. *Acta Crystallogr.* 2015, A71, 3-8.
- [14] Sheldrick G. M. *Acta Crystallogr.* 2015, C71, 3-8.
- [15] Dolomanov O. V., Bourhis L. J., Gildea R. J., Howard J. A. K., Puschmann H. *J. Appl. Crystallogr.* 2009, 42, 339-341.