Synthesis, Characterization and Crystal Structure of a Binuclear Cadmium Iodide Complex with a Multi-*N*-donor Oxazolidine Ligand

Mohammad Hakimi[a], Zahra Mardani[a], Keyvan Moeini[a], Mao Minoura[b], and Heidar Raissi[c]

[a] Chemistry Department, Payame Noor University, 19395-4697 Tehran, Iran
[b] Department of Chemistry, School of Science, Kitasato University, 1-15-1 Kitasato, minami-ku, Sagamihara, Kanagawa 252-0373, Japan
[c] Chemistry Department, Birjand University, Shokat Abad-Pardis-e-Daneshgah, Birjand, South Khorasan 13179, Iran

Reprint requests to Mohammad Hakimi. E-mail: mohakimi@yahoo.com

Z. Naturforsch. **2011**, *66b,* 1122 – 1126; received August 4, 2011

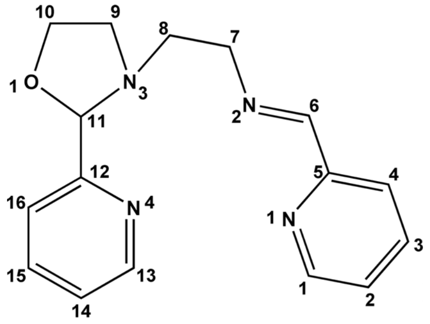
The ligand, 2-(2-(pyridin-2-yl)oxazolidin-3-yl)-*N*-(pyridin-2-ylmethylene)ethanamine, POPME, was prepared *via* microwave-supported Schiff base and oxazolidination reactions. The cadmium iodide complex $[Cd_2(POPME)(\mu\text{-}I)_2I_2]$ was prepared and identified by elemental analysis, IR, Raman and ^1H and ^{13}C NMR spectroscopy and single-crystal X-ray diffraction. In the crystal structure two Cd(II) ions with coordination numbers four and six are bridged by two iodide anions. Cd1 and Cd2 have distorted octahedral CdI_2N_4 and tetrahedral CdI_4 geometries, respectively. Weak intermolecular hydrogen bonds H···I and H···O stabilize the supramolecular network.

Key words: X-Ray Crystal Structure, Cadmium, Oxazolidine Ligand, Bridging Iodide

Introduction

Oxazolidine moieties are present in many biologically active molecules of pharmaceutical interest [1 – 3]. These ring systems have been exploited successfully in medicinally valuable compounds such as the anticancer prodrugs doxazolidine, doxoform, and doxaz carbamate [4]. Oxazolidine derivatives have also been investigated extensively because of their importance as chiral auxiliaries in the synthesis of a variety of chiral compounds. Amino alcohols react with aldehydes or asymmetric ketones to produce chiral compounds [5]. In addition to reactions of amino alcohols with carbonyl compounds [6 – 8], there are other routes for the preparation of oxazolidines [9 – 11].

In the past few years, we have prepared a series of new *N*-donor ligands and studied the complexation of 3,4-diamino-5-methyl-4H-1,2,4-triazole (DAMT), 4-amino-1,2,4-triazoline-5-thione (HATT), 4-amino-1,2,4-triazin-3(2H)-thione-5-one (ATTO), and 4-amino-5-methyl-1,2,4-triazol-3(2H)-thione (HAMTT) with copper(I), silver(I) and cadmium(II) [12 – 17].



Scheme 1. The structure of POPME.

In this paper, we present the synthesis and spectroscopic characterization of the ligand 2-(2-(pyridin-2-yl)oxazolidin-3-yl)-*N*-(pyridin-2-ylmethylene)ethanamine, POPME (Scheme 1). Furthermore, its cadmium iodide complex $[Cd_2(POPME)(\mu\text{-}I)_2I_2]$, **1**, has been synthesized and its crystal structure has been determined.

Results and Discussion

The racemic POPME ligand was prepared in high yield *via* Schiff base and oxazolidination reactions by treating 2-(2-aminoethylamino)ethanol with pyridine-2-carbaldehyde in a microwave reactor under solvent-free conditions. POPME is an interesting tetra-dentate asymmetric ligand with an oxazolidine and two pyridine rings containing three different types of donor

$$2\ \mathrm{CdI_2} + \mathrm{POPME} \xrightarrow{\text{Ethanol}/\Delta} [\mathrm{Cd_2(POPME)}(\mu\text{-I})_2\mathrm{I_2}]$$

Scheme 2. Synthesis of **1**.

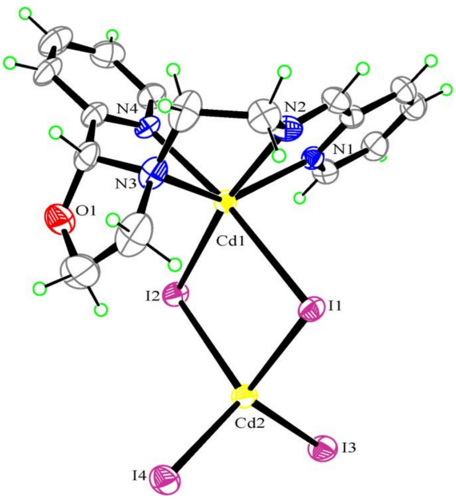


Fig. 1 (color online). ORTEP-III drawing of the molecular structure of $[\mathrm{Cd_2(POPME)}(\mu\text{-I})_2\mathrm{I_2}]$ (**1**) in the crystal. The displacement ellipsoids are drawn at the 30 % probability level.

centers: two pyridine nitrogen atoms, an aliphatic tertiary amine, and an imine group.

Reaction of POPME with an ethanolic solution of cadmium(II) iodide with a molar ratio of 1 : 2 resulted in the growth of colorless crystals of **1** (Scheme 2). The complex was air-stable, and soluble in methanol, DMF and DMSO.

The frequencies of the IR bands for the free ligand were different from those of the corresponding complex and provided significant indications regarding the bonding sites of the POPME ligand. For the complex, $\nu(\mathrm{C{=}N})_{\mathrm{imine}}$ is shifted by 39 $\mathrm{cm^{-1}}$ above of that of the free ligand indicating that the nitrogen atom of the imine participates in the coordination. The ring wagging vibrations of the pyridine groups were observed at 617 and 756 $\mathrm{cm^{-1}}$ for POPME and at 640 and 771 $\mathrm{cm^{-1}}$ for **1**. In the IR and Raman spectra of **1**, the bands at 520 and 524 $\mathrm{cm^{-1}}$ are due to Cd-N stretching vibrations.

Information about the low-frequency vibrations of metal-halide and metal-ligand bonds can be obtained by Raman spectroscopy. The terminal Cd-I stretching vibration has been assigned to the strong band at 182 $\mathrm{cm^{-1}}$ for the complex consistent with the values reported in the literature (100 – 200 $\mathrm{cm^{-1}}$) for $\mathrm{CdI_2}$. The stretching frequency for bridging Cd-I unit appear around 100 $\mathrm{cm^{-1}}$, lower than the stretching frequency of terminal Cd-I unit [18].

The numbering scheme used for the ^{1}H NMR and ^{13}C NMR spectra of the free ligand is given in Scheme 1, and data are given in the Experimental Section. In the ^{1}H NMR spectrum, the $\mathrm{C^{11}H}$ signal appears at 4.9 ppm. After coordination, this signal is shifted by 0.6 ppm to lower magnetic field. Similar shifts were observed for the $\mathrm{CH_2N}$ signals.

The ORTEP-III diagrams for the crystal structure of **1** are shown in Figs. 1 and 2. Single-crystal X-ray analysis revealed that in this asymmetric binuclear complex the two cadmium atoms have different coordination numbers. A search for similar structures with CONQUEST [19] has revealed that this type of coordination is unique for cadmium. The coordination numbers in Cd1 and Cd2 are six and four, respectively. Cd1 is coordinated by the tetradentate ligand forming

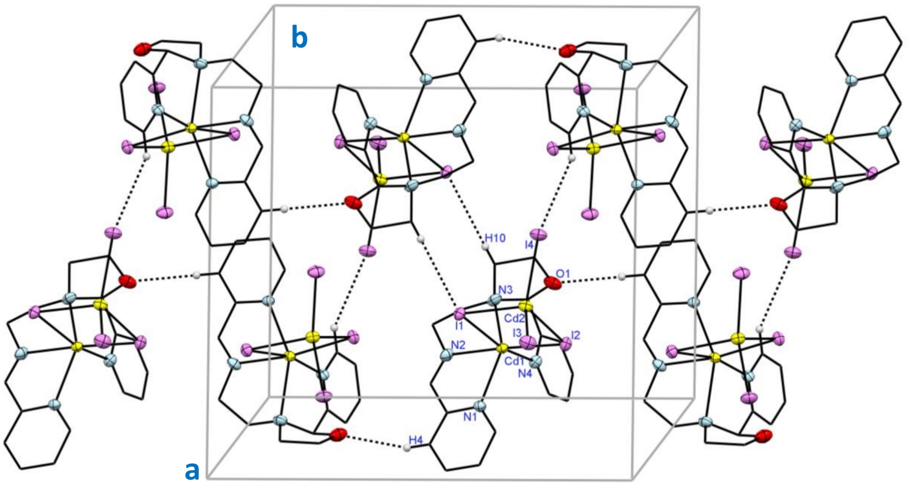


Fig. 2 (color online). Crystal structure of complex **1**, showing the hydrogen-bonded chain formation along the crystallographic *b* direction.

Table 1. Selected bond lengths (Å) and angles (deg) for **1** with estimated standard deviations in parentheses.

Cd1–N1	2.388(6)	Cd1–N2	2.302(7)
Cd1–N3	2.466(6)	Cd1–N4	2.335(6)
Cd1–I1	3.0238(8)	Cd1–I2	2.8559(8)
Cd2–I1	2.8384(9)	Cd2–I2	2.8785(9)
Cd2–I3	2.7206(9)	Cd2–I4	2.7325(10)
N2–Cd1–N4	96.4(2)	N4–Cd1–N3	71.3(2)
N2–Cd1–I2	170.41(18)	N2–Cd1–I1	82.98(18)
I2–Cd1–I1	90.41(3)	I3–Cd2–I4	119.44(3)
I4–Cd2–I1	104.43(3)	I4–Cd2–I2	113.19(3)
I3–Cd2–I4	119.44(3)		

Table 2. Dimensions of the weak hydrogen bonds (Å, deg) in **1**.

D–H···A	*d*(D–H)	*d*(H···A)	∠(DHA)	*d*(D···A)
C13–H15···I4	0.931	3.158	147.64	3.975(9)
C9–H10···I1	0.971	3.164	140.41	3.96(1)
C15–H17···I1	0.930	3.107	146.29	3.91(1)
C4–H4···O1	0.930	2.623	146.88	3.44(1)

three five-membered chelate rings. Only the chelate rings containing N1 and N2 are planar. The distorted octahedral coordination of Cd1 is completed by two iodide atoms (I1 and I2). The terminal I^- anions (I3 and I4) act as monodentate ligands with different Cd–I bond lengths. This difference in bond lengths can be attributed to the participation of I4 in intermolecular hydrogen bonds. Two iodide anions (I1 and I2) bridge the Cd1 and Cd2 atoms. The Cd1–I1 bond is longer than the Cd1–I2 bond, and the terminal Cd–I bond lengths are shorter than the bridging Cd–I bond lengths. The bond angles listed in Table 1 prove that the geometry of Cd2 is tetrahedral. The dihedral angle between the N1 pyridine ring and the N2 chelate ring is 1.50°, which means that these rings are coplanar. The crystal structure of **1** is three-dimensional (Fig. 2) *via* very weak I···H and O···H hydrogen bonds. I1, I4 and O1 act as proton acceptors (I1 as a double proton acceptor), while C4, C9, C13, and C15 are proton donors (Table 2).

Conclusion

The preparation of the tetradentate ligand POPME and its complex $[Cd_2(POPME)(\mu\text{-}I)_2I_2]$ have been presented. The X-ray crystallography of **1** showed a distorted octahedral geometry for Cd1 and a distorted tetrahedral geometry for Cd2. Two Cd(II) ions are bridged by two iodide anions, leading to an asymmetrical binuclear complex. In the crystal of **1**, weak H···I and H···O hydrogen bonds gave rise to a supramolecular network. In continuation of our research, we will plan to prepare and structurally characterize further complexes of the POPME ligand.

Experimental Section

Materials and instrumentation

All starting chemicals and solvents were reagent or analytical grade and used as received. The infrared spectra of a KBr pellet were recorded in the range 4000 – 400 cm^{-1} with a FT-IR 8400-Shimadzu spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Brucker Aspect 3000 instrument operating at 300 MHz; chemical shifts are given in parts per million, with values in reference to an internal standard of TMS. The carbon, hydrogen, and nitrogen contents were determined in a Thermo Finnigan Flash Elemental Analyzer 1112 EA. The microwave-assisted reaction was carried out using a Microwave Laboratory Systems MicroSYNTH. Raman spectra were performed using a Nicolet Model 910 Fourier-transform spectrometer. The excitation was the near-IR line at 1.064 μm (or 9398.5 cm^{-1}) from a 3 W cw Nd : YAG laser. About 2000 scans at a resolution of 2 cm^{-1} were recorded to ensure a high signal-to-noise ratio. Melting points were determined with a Barnsted Electrothermal 9200 electrically heated apparatus.

2-(2-(Pyridin-2-yl)oxazolidin-3-yl)-N-(pyridin-2-ylmethylene)ethanamine, POPME

A mixture of 0.21 g (2 mmol) of pyridine-2-carbaldehyde and 0.10 g (1 mmol) 2-(2-amino-ethylamino)ethanol was irradiated inside a microwave oven for 10 min with a power up to 1 kW. After microwave irradiation, an oily liquid was obtained and washed with diethyl ether. Several attempts to crystallize the compound were unsuccessful. $C_{16}H_{18}N_4O$ (282.34): calcd. C 68.06, H 6.43, N 19.84; found C 68.01, H 6.33, N 20.11. – IR (KBr disc): ν = 3055 $(CH)_{ar}$, 2900 (CH_2), 1635 (C=N), 1589 $(C{=}N)_{py}$, 1533 (C=C), δ_{as} = 1466 (CH_2), δ_s = 1366 (CH_2), ν = 1242 (C-O), 1149 (C-N), γ = 756 and 617 (py) cm^{-1}. – ^1H NMR (300 MHz, $[D_6]$DMSO): δ = 1.0 (t, 2 H, C^7H_2); 2.5 – 3.9 (m, 6 H, CH_2); 4.9 (s, 1 H, $C^{11}H$); 7.2 – 8.6 (m, 9 H, CH_{py}, C^6H). – ^{13}C NMR (300 MHz, $[D_6]$DMSO): δ = 51.5 (C^9), 51.9 (C^8), 52.4 (C^7), 65.9 (C^{10}), 97.2 (C^{11}), 120.1 (C^{14}), 123.9 (C^4), 125.5 (C^{16}), 126.8 (C^2), 136.9 (C^3), 137 (C^{15}), 148.7 (C^{13}), 149.0 (C^1), 163.0 (C^5, C^{12}).

Diiodo(di-μ-iodo)-2-(2-(pyridin-2-yl)oxazolidin-3-yl)-N-(pyridin-2-ylmethylene) ethanamine-dicadmium(II), $[Cd_2(POPME)(\mu\text{-}I)_2I_2]$, (1)

A solution of 0.28 g (1 mmol) of POPME, dissolved in EtOH (15 mL), was added with stirring to a solution of 0.72 g (2 mmol) of CdI_2 in EtOH (25 mL). The reaction mixture was stirred at 60 °C for 12 h. Colorless crystals suitable for

Table 3. Crystal data and parameters pertinent to data collection and structure refinement of **1**.

Formula	$C_{16}H_{18}Cd_2I_4N_4O$
M_r	1014.74
Crystal size, mm^3	$0.30 \times 0.20 \times 0.05$
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	10.727(3)
b, Å	15.413(4)
c, Å	15.896(4)
β, deg	104.028(3)
V, Å^3	2549.8(11)
Z	4
D_{calcd}, g cm^{-3}	2.64
μ(MoK_α), cm^{-1}	6.5
F(000), e	1832
h,k,l range	$-13 \le h \le 9$, $-19 \le k \le 19$, $-10 \le l \le 20$
Refl. measured / unique / R_{int}	12728 / 5534 / 0.041
Param. refined	244
$R(F)$ / $wR(F^2)$ (all refl.)	0.043 / 0.137
GoF (F^2)	1.074
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	2.07 / −1.54

X-ray diffraction were obtained from the solution after standing for 2 d. M. p. 239 °C. – $C_{16}H_{18}Cd_2I_4N_4O$ (1014.78): calcd. C 18.94, H 1.79, N 5.52; found C 19.00, H 1.81, N 5.7. – IR (KBr disc): ν = 3062 $(CH)_{ar}$, 2900 (CH_2), 1674 (C=N), 1597 $(C{=}N)_{py}$, 1531 $(C{=}C)_{ar}$, δ_{as} = 1442 (CH_2), δ_s = 1389 (CH_2), 1218 (C-O), 1074 (C-N), γ = 771 and 640 (py), ν = 520 (Cd-N) cm^{-1}. – Raman (Raman shift): ν = 3059 $(CH)_{ar}$, 2903 (CH_2), 1601 $(C{=}N)_{py}$, 1528 $(C{=}C)_{ar}$, 1214 (C-O), 1076 (C-N), γ = 679 (py), ν = 524 $(Cd\text{-}N)_{imine}$, 401 $(Cd\text{-}N)_{py}$, 303 (N-Cd-N), 182 $(Cd\text{-}I)_{terminal}$ cm^{-1}. – ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 1.2 (t, 2 H, C^7H_2), 2.8 – 4.1 (m, 6 H, CH_2), 5.48 (s, 1 H, $C^{11}H$), 7.5 – 9.0 (m, 9 H, CH_{py}, C^6H).

X-Ray structure determination

The data collection for **1** was carried with a Bruker APEX-II CCD diffractometer, using graphite-monochromatized MoKα (λ = 0.71073 Å) radiation at 296 K. The data were integrated with SAINT [20] and corrected for Lorentz and polarization effects. Absorption was corrected for using SADABS [21]. The structure was solved by Patterson methods, implemented in SHELXS-97 [22]. Refinement by full-matrix least squares methods based on F^2 values against all reflections has been performed by SHELXL-97 [22], including anisotropic displacement parameters for all non-H atoms. The position of hydrogen atoms belonging to the carbon atoms Csp^2 were geometrically optimized applying the riding model [Csp^2–H, 0.93 Å; U_{iso}(H) = 1.2 U_{eq}(C)]. Calculations concerning the molecular geometry, the verification of space group and the analysis of hydrogen bonds were performed with PLATON [23]. The molecular graphics were drawn with ORTEP-III [24] and MERCURY (version 2.3) [25]. Crystallographic data and details of the data collection and structure refinement are listed in Table 3. Bond lengths (Å) and angles (deg) are reported in Table 1, and the hydrogen bonding geometry in Table 2.

CCDC 835283 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

---

[1] K. Ii, S. Ichikawa, B. Al-Dabbagh, A. Bouhss, A. Matsuda, *J. Med. Chem.* **2010**, *53*, 3793 – 3813.

[2] M. Keller, C. Boissard, L. Patiny, N. N. Chung, C. Lemieux, M. Mutter, P. W. Schiller, *J. Med. Chem.* **2001**, *44*, 3896 – 3903.

[3] G. Tuchscherer, D. Grell, Y. Tatsu, P. Durieux, J. Fernandez-Carneado, B. Hengst, C. Kardinal, S. Feller, *Angew. Chem.* **2001**, *113*, 2930 – 2934. *Angew. Chem. Int. Ed.* **2001**, *40*, 2844 – 2848.

[4] J. Wang, F. D. Rochon, Y. Yang, L. Huac, M. M. Kayser, *Tetrahedron* **2007**, *18*, 1115 – 1123.

[5] D. A. Evans, *Aldrichim. Acta* **1982**, *15*, 23.

[6] Y.-F. Kang, R. Wang, L. Liu, C.-S. Da, W.-J. Yana, Z.-Q. Xua, *Tetrahedron* **2005**, *46*, 863 – 865.

[7] E. Błocka, M. Jaworska, A. Kozakiewicz, M. Wełniak, A. Wojtczak, *Tetrahedron* **2010**, *21*, 571 – 577.

[8] R. S. B. Gonçalves, C. R. Kaiser, M. C. S. Lourenço, M. V. N. de Souza, J. L. Wardell, S. M. S. V. Wardell, A. D. da Silva, *Eur. J. Med. Chem.* **2010**, *45*, 6095 – 6100.

[9] O. Merino, B. M. Santoyo, L. E. Montiel, H. A. Jiménez-Vázquez, L. Gerardo Zepeda, J. Tamariz, *Tetrahedron* **2010**, *51*, 3738 – 3742.

[10] N. Gandhi, B. K. Srivastava, V. B. Lohray, B. B. Lohray, *Tetrahedron* **2004**, *45*, 6269 – 6272.

[11] M. Mohammadizadeh, N. Firoozi, *Tetrahedron* **2010**, *51*, 2467 – 2469.

[12] M. Hakimi, M. Maeder, G. A. Lawrance, *J. Coord. Chem.* **2011**, *64*, 105 – 114.

[13] M. Hakimi, M. H. Vahedi, M. Rezvaninezhad, E. Schuh, F. Mohr, *J. Sulfur Chem.* **2011**, *32*, 55 – 61.

[14] M. Hakimi, M. Yazdanbakhsh, M. M. Heravi, M. Ghassemzadeh, B. Neumüller, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1899 – 1902.

[15] M. Yazdanbakhsh, M. Hakimi, M. M. Heravi, M. Ghassemzadeh, B. Neumüller, *Z. Anorg. Allg. Chem.* **2004**, *630*, 627 – 629.

[16] M. Yazdanbakhsh, M. Hakimi, M. M. Heravi, M. Ghassemzadeh, B. Neumüller, *Z. Anorg. Allg. Chem.* **2005**, *631*, 924 – 927.

[17] M. Yazdanbakhsh, M. Hakimi, M. M. Heravi, R. Boese, *Z. Anorg. Allg. Chem.* **2006**, *632*, 2201–2203.

[18] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, **1986**, pp. 324–328.

[19] CONQUEST 1.13, Copyright Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, **2011**.

[20] SAINT (version 7.12), Bruker Analytical X-ray Instruments Inc., Madison, Wisconsin (USA) **2004**.

[21] G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Göttingen (Germany) **1996**.

[22] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473; *ibid.* **2008**, *A64*, 112–122.

[23] A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, Utrecht (The Netherlands) **2010**. See also: A. L. Spek, *J. Appl. Crystallogr.* **2009**, *D65*, 148–155.

[24] C. K. Johnson, M. N. Burnett, ORTEP-III, Oak Ridge Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Rep. ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN (USA) **1996**. Windows version: L. J. Farrugia, University of Glasgow, Glasgow, Scotland (U.K.) **1999**. See also: L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

[25] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood, *J. Appl. Crystallogr.* **2008**, *41*, 466–470.