Polyhedron 49 (2013) 19-23

Contents lists available at SciVerse ScienceDirect

Polyhedron



journal homepage: www.elsevier.com/locate/poly

Zinc(II) and mercury(II) complexes $[Zn((2,6-Cl-ba)_2en)I_2]$ and $[Hg((2,6-Cl-ba)_2en)Br_2]$ with the bidentate Schiff base ligand $(2,6-Cl-ba)_2en$: Synthesis, characterization and crystal structures

Aliakbar Dehno Khalaji ^{a,*}, Gholamhossein Grivani ^b, Mohammad Seyyedi ^b, Karla Fejfarova ^c, Michal Dusek ^c

^a Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran ^b School of Chemistry, Damghan University, Damghan, P.O. Box 36715-364, Iran ^c Institute of Physics of the ASCR, v.v.i., Na Slovance 2, 182 21 Prague 8, Czech Republic

ARTICLE INFO

Article history: Received 31 July 2012 Accepted 26 September 2012 Available online 8 October 2012

Keywords: Zinc(II) Mercury(II) Schiff base Single-crystal: tetrahedral

1. Introduction

The coordination chemistry of zinc(II) and mercury(II) complexes containing Schiff base ligands has been of interest in recent years [1–9], because of its important role in the development of coordination chemistry. These complexes have widely used photoluminescent properties [10] and they can also be utilized for the construction of coordination polymers and networks [11–15]. Although the polymeric coordination chemistry of zinc(II) and mercury(II) with Schiff base ligands has been extensively studied [6,8,9,11–15], data on mononuclear zinc(II) and mercury(II) complexes are relatively scarce [1–5,7,10].

In a continuation of our work on the preparation of zinc(II) and mercury(II) complexes with symmetric bidentate Schiff base ligands [16–20], here we report the synthesis, spectroscopic studies and crystal structures of zinc(II) and mercury(II) complexes with the Schiff base ligand (2,6-Cl-ba)₂en (Scheme 1).

2. Experimental

2.1. Materials and methods

All reagents and solvents for the syntheses and analyses were commercially available and used as received without further

ABSTRACT

The zinc(II) and mercury(II) complexes $[Zn((2,6-Cl-ba)_2en)I_2]$ (1) and $[Hg((2,6-Cl-ba)_2en)Br_2]$ (2) were prepared from the reaction of zinc(II) iodide and mercury(II) bromide with the bidentate Schiff base ligand (2,6-Cl-ba)_2en, having the systematic name [N,N'-bis(2,6-dichlorobenzylidene)ethane-1,2-dia-mine]. The two complexes were characterized by elemental analysis (CHN), FT-IR spectroscopy and X-ray single-crystal diffraction. The crystal structure analysis revealed that the coordination geometry around the metal ions in the two complexes is distorted tetrahedral. The Schiff base ligand (2,6-Cl-ba)_2en acts as a chelating ligand and coordinates via two nitrogen atoms to the metal centers.

© 2012 Elsevier Ltd. All rights reserved.

purifications. Infrared spectra were recorded using KBr disks on a FT-IR Perkin–Elmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN-O-Rapid analyzer. ¹H NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz. All chemical shifts are reported in δ units downfield from TMS.

2.2. Preparation of (2,6-Cl-ba)₂en

 $(2,6-Cl-ba)_2$ en was prepared by the condensation of 2,6-dichlorobenzaldehyde with ethane-1,2-diamine following method described in [21]. Yield: 92%. *Anal.* Calc. for C₁₆H₁₂N₂Cl₄: C, 51.37; H, 3.23; N, 7.49. Found: C, 51.40; H, 3.29; N, 7.55%. IR (KBr pellet, cm⁻¹): 1641 (s, C=N).

2.3. Preparation of $[Zn((2,6-Cl-ba)_2en)I_2]$ (1)

To a stirring solution of the Schiff base ligand $(2,6-Cl-ba)_2$ en (0.0374 g, 1 mmol) in 15 ml of chloroform was added Znl₂ (0.0319 g, 1 mmol) in 15 ml of hot methanol. The mixture was stirred for 0.5 h in air at 25 °C and then left at room temperature for several days without disturbance, yielding micro crystals of **1**. Yield: 78%. *Anal.* Calc. for C₁₆H₁₂N₂Cl₄Znl₂: C, 27.72; H, 1.74; N, 4.04. Found: C, 27.80; H, 1.85; N, 4.11%. IR (KBr pellet, cm⁻¹): 1648 (s, C=N).



^{*} Corresponding author. Tel./fax: +98 171 4427050.

E-mail addresses: alidkhalaji@yahoo.com, ad.khalaji@gu.ac.ir (A.D. Khalaji).

^{0277-5387/\$ -} see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2012.09.054



Scheme 1. Chemical structures of Schiff base ligand (2,6-Cl-ba)₂en and its zinc(II) and mercury(II) complexes.

2.4. Preparation of $[Hg((2,6-Cl-ba)_2en)Br_2]$ (2)

To a stirring solution of the Schiff base ligand $(2,6-Cl-ba)_2$ en (0.0374 g, 1 mmol) in 15 ml of chloroform was added HgBr₂ (0.0361 g, 1 mmol) in 15 ml of hot methanol. The mixture was stirred for 0.5 h in air at 50 °C and then left at room temperature for several days without disturbance, yielding micro crystals of **2**. Yield: 70%. *Anal.* Calc. for C₁₆H₁₂N₂Cl₄HgBr₂: C, 26.16; H, 1.65; N, 3.81. Found: C, 26.22; H, 1.71; N, 3.89%. IR (KBr pellet, cm⁻¹): 1663 (s, C=N).

2.5. Crystallography data collection and refinement

Suitable single crystals of **1** and **2** were chosen for an X-ray diffraction study. Crystallographic measurements were done at 120 K with a four circle CCD diffractometer, Gemini of Oxford Diffraction Ltd. For **1**, mirror-collimated Cu K α radiation ($\lambda = 1.5418$ Å) was used. The corresponding absorption coefficient was large (see Table 1), but absorption corrections based on the crystal shape, combined with absorption corrections based on the spherical

Table 1

Crystallographic data and structure refinement for 1 and 2.

	1	2
Chemical formula	$C_{16}H_{12}Cl_4I_2N_2Zn$	C ₁₆ H ₁₂ Br ₂ Cl ₄ HgN ₂
Formula weight	693.3	734.5
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$	ΡĪ
Ζ	4	4
T (K)	120	120
a (Å)	11.1234(6)	8.2209(4)
b (Å)	13.9349(6)	14.8315(7)
<i>c</i> (Å)	13.7380(6)	18.4452(8)
α (°)	90	72.086(4)
β(°)	90.350(4)	83.081(4)
γ (°)	90	78.056(4)
<i>V</i> (Å ³)	2129.40(17)	2089.73(18)
Wavelength	Cu Kα	Μο Κα
T _{min}	0.075	0.055
T _{max}	0.511	0.112
μ (mm ⁻¹)	29.01	11.70
Measured reflections	11059	31.271
Independent reflections	3751	10230
Reflection with $I > 3\sigma(I)$	3170	7444
R _{int}	0.030	0.032
S	1.72	1.16
$R[F^2 > 2\sigma(F^2)]$	0.031	0.027
$wR(F^2)$	0.076	0.062
Parameters	226	451
$\Delta \rho_{\rm max} ({\rm e}{\rm \AA}^{-3})$	0.91	0.89
$\Delta ho_{\min} (e \text{\AA}^{-3})$	-0.62	-0.65
Crystal size (mm ³)	$0.36 \times 0.08 \times 0.03$	$0.41 \times 0.39 \times 0.31$

harmonic functions successfully corrected for this effect. The strongly absorbing compound **2** was measured with graphitemonochromated Mo K α radiation ($\lambda = 0.7107$ Å). The crystal structures were solved by direct methods with the program SIR2002 [22] and refined with the JANA2006 program package [23] by the full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by ORTEP III [24]. Hydrogen atoms were mostly discernible in the difference Fourier maps and could be refined to a reasonable geometry. According to common practice they were nevertheless kept in ideal positions during the refinement. The isotropic atomic displacement parameters of the hydrogen atoms were evaluated as $1.2-1.5 U_{eq}$ of the parent atom. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

3. Results and discussion

3.1. Synthesis and characterization

The reaction between (2,6-Cl-ba)₂en and zinc(II) iodide or mercury(II) bromide provided monomeric zinc(II) and mercury(II) complexes, [Zn((2,6-Cl-ba)₂en)l₂] (1) and [Hg((2,6-Cl-ba)₂en)Br₂] (2). The complexes are moderately soluble in common organic solvents such as methanol, ethanol, chloroform, dichloromethane and acetone, and are completely soluble in coordinating solvents such as DMF and DMSO. In order to confirm the chemical composition of both complexes, elemental analysis (CHN) was carried out on the crystallized compounds.

The FT-IR spectra of the free ligand $(2,6-Cl-ba)_2$ en and the complexes exhibit a characteristic band of the C=N group, which appears at 1641 cm⁻¹ for the ligand and is shifted in the complexes to 1648 (**1**) and 1663 cm⁻¹ (**2**), due to the coordination of the azomethine group.

3.2. Crystal and molecular structure of 1

An ORTEP view of **1** with the atom-numbering scheme is presented in Fig. 1. Selected bond distances and angles are given in Table 2. As shown in Fig. 1, each zinc(II) ion is coordinated with two iminic nitrogen atoms from the Schiff base ligand (2,6-Cl-ba)₂en and two iodine atoms in the form of strongly deformed tetrahedron. The organic Schiff base ligand acts as a chelating bidentate ligand. The geometry around the zinc(II) center of this complex is quite similar to the zinc(II) complexes $[Zn((3,4-MeO-ba)_2en)I_2]$ [20], $[Zn((2,3-MeO-ba)_2en)I_2]$ [16] and $[Zn((2,3,4-MeO-ba)_2en)I_2]$ [18]. The Schiff base ligands (3,4-MeO-ba)₂en, (2,3-MeO-ba)₂en and (2,3,4-MeO-ba)₂en in previous complexes [16,18,20] adopt a *Z,Z* configuration around the iminic group, but in this complex, the



Fig. 1. An ORTEP view of 1 with the atom-numbering scheme. Atomic displacement parameters are shown at the 50% probability level.

Table 2Selected bond distances (Å) and angles (°) of 1.

	., .	·	
I1-Zn1	2.5258(7)	I2-Zn1	2.5460(8)
Zn1-N1	2.103(5)	Zn1-N2	2.098(4)
N1-C1	1.478(8)	N1-C2	1.256(8)
N2-C9	1.467(8)	N2-C10	1.249(7)
C1-C9	1.470(10)	C2-C3	1.474(8)
C10-C11	1.488(7)		
I1-Zn1-I2	120.69(3)	N1-Zn1-N2	81.07(17)
I1-Zn1-N1	112.22(13)	N1-Zn1-I2	114.03(13)
I1-Zn1-N2	115.11(13)	N2-Zn1-I2	106.93(12)
Zn1-N1-C1	107.3(4)	Zn1-N1-C2	133.3(4)
Zn1-N2-C9	109.9(4)	Zn1-N2-C10	129.1(4)
N1-C1-C9	108.8(5)	N1-C2-C3	122.5(5)
N2-C9-C1	108.0(5)	N2-C10-C11	126.3(5)

Table 3					
Inter-molecular	hydrogen	bond	geometry	for	1

C1–H (Å)	H···I1 (Å)	C1…I1 (Å)	C1−H· · ·I1 (°)
0.960	3.135	4.041	157.847

I1 (x, 0.5 – y, 0.5 + z).

Schiff base ligand $(2,6-Cl-ba)_2$ en adopts a *Z*,*E* configuration around the iminic group (Fig. 1).

The geometry of the hydrogen bonds in **1** is given in Table 3. Complex **1** exhibits one hydrogen bonding pattern built up from non-classical C-H \cdots I interactions (Fig. 2).

3.3. Crystal and molecular structure of 2

An ORTEP view of **2** with the atom-numbering scheme is presented in Fig. 3. Selected bond distances and angles are given in Table 4. The single crystal X-ray analysis has revealed that the mercury(II) complex $[Hg((2,6-CI-ba)_2en)Br_2]$ (**2**) is neutral and crystallizes in triclinic space group $P\overline{1}$. Mercury(II) is coordinated by two iminic nitrogen atoms of the chelating bidentate Schiff-base ligand (2,6-CI-ba)_2en and two bromine atoms in a form of strongly deformed tetrahedron. The geometry around the mercury(II) comter of this complex is quite similar to the mercury(II) complexes $[Hg((2,3-MeO-ba)_2en)Br_2]$ [19] and $[Hg((Me-ca)_2en)Br_2]$ [17]. The Schiff base ligands (2,3-MeO-ba)_2en and (Me-ca)_2en in previous complexes [17,19] and (2,6-CI-ba)_2en in this complex adopt a *Z*,*Z* configuration around the iminic group (Fig. 3).

Although a tetrahedral geometry might be expected for four coordinated zinc(II) and mercury(II) centers, it is distorted by the



Fig. 2. Non-classical C-H...I hydrogen bond in complex 1 (dashed lines).

restricting bite chelate angle N1–Zn1–N2 81.07(17)°, N1–Hg1–N2 70.43(13)° and N3–Hg2–N4 71.13(13)° of the Schiff-base ligand. For ethylenediamine chelate compounds [16–20] this angle ranges between 82° and 89°, i.e. significantly below 109.5°. On the contrary the I1–Zn1–I2, Br1–Hg1–Br2 and Br3–Hg2–Br4 angle has opened up to 120.69(3)°, 138.121(16)° and 128.645(16)°, respectively. The N–Zn–I angles are also distorted from the tetrahedral values (Table 2 for **1** and Table 3 for **2**). The Zn1–N1, Zn1–N2, Hg1–N1, Hg1–N2, Hg2–N3 and Hg2–N4 bond lengths of 2.103(5), 2.098(4), 2.507(4), 2.462(3), 2.540(6) and 2.368(4) Å and Zn1–I1, Zn1–I2, Hg1–Br1, Hg1–Br2, Hg2–Br3 and Hg2–Br4 bond lengths of 2.5258(7), 2.5460(8), 2.5067(5), 2.4615(5), 2.5401(5) and



Fig. 3. An ORTEP view of 2 with the atom-numbering scheme. Atomic displacement parameters are shown at the 50% probability level.

Table 4						
Selected	bond	distances	(Å) and	angles	(°)	of 2 .

Hg1-Br1	2.5067(5)	Hg1-Br2	2.4615(5)
Hg2–Br3	2.5401(5)	Hg2–Br4	2.4578(5)
Hg1–N1	2.507(4)	Hg1–N2	2.462(3)
Hg2–N3	2.540(6)	Hg2–N4	2.368(4)
N1-C10	1.259(6)	N1-C1	1.467(6)
N2-C3	1.267(6)	N2-C2	1.458(5)
N3-C26	1.260(6)	N3-C17	1.469(6)
N4-C18	1.464(5)	N4-C19	1.266(6)
C3-C4	1.466(5)	C10-C11	1.482(6)
C1-C2	1.520(7)	C17-C18	1.516(7)
C26-C27	1.483(7)	C19-C20	1.474(5)
N1-Hg1-N2	70.43(13)	N3-Hg2-N4	71.13(13)
Br1-Hg1-Br2	138.121(16)	Br3-Hg2-Br4	128.645(16)
Br1-Hg1-N1	93.60(5)	Br3–Hg2–N3	95.98(5)
Br1-Hg1-N2	100.57(5)	Br3-Hg2-N4	96.18(7)
Br2-Hg1-N1	119.87(4)	Br4–Hg2–N3	124.56(5)
Br2-Hg1-N2	113.38(5)	Br4–Hg2–N4	124.07(7)
Hg1-N2-C3	132.15(5)	Hg2-N4-C19	132.0(3)
Hg1-N1-C10	126.21(10)	Hg2-N3-C26	126.23(5)
N2-C3-C4	123.5(4)	N4-C19-C20	121.5(4)
N2-C2-C1	108.8(4)	N4-C18-C17	107.4(3)
N1-C10-C11	122.3(4)	N3-C26-C27	121.5(4)
N1-C1-C2	110.6(3)	N3-C17-C18	110.0(3)

2.4578(5) Å are similar to the corresponding distances in other tetrahedral zinc(II) and mercury(II) complexes [16–20]. The geometry about the metal centers in these complexes is also approximately tetrahedral, with the distortion indicated by the unequal metal–ligand bond distances and angles [16–20].

Acknowledgments

We acknowledge Golestan University (GU) and Damghan University (DU) for partial support of this work, and the project

P204/11/0809 of the Grant Agency of the Czech Republic for supporting the crystallographic part.

Appendix A. Supplementary data

CCDC 902030 and 902031 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] M. Motazerozohori, S. Joohari, S.A. Musavi, J. Coord. Chem. 62 (2009) 1285.
- [2] S. Dehghanpour, A. Mahmoudi, Synth. React. Inorg. Met.-Org. Nano-Met. Chem.
- 37 (2007) 35.
 [3] M. Amirnasr, A.H. Mahmoudkhani, A. Gorji, S. Dehghanpour, H.R. Bijanzadeh, Polyhedron 21 (2002) 2733.
- [4] K. Marjani, J. Asgarian, M. Mousavi, V. Amani, Z. Anorg. Allg. Chem. 635 (2009) 1633.
- 5] M. Motazerozohori, S.A. Musavi, J. Coord. Chem. 61 (2008) 3934.
- [6] G. Mahmoudi, A. Morsali, CrystEngComm. 11 (2009) 50.
- [7] M. Motazerozohori, S. Joohari, S.A. Musavi, Spectrochim. Acta A73 (2009) 231.
- [8] G. Mahmoudi, A. Morsali, A.D. Hunter, M. Zeller, CrystEngComm. 9 (2007) 704.
- [9] M.G.B. Drew, S. De, D. Datta, Inorg. Chim. Acta 362 (2009) 2487.
- [10] R. Fan, Y. Yang, Y. Yin, W. Hasi, Y. Mu, Inorg. Chem. 48 (2009) 6034.
- [11] M. Ghoreishi Amiri, G. Mahmoudi, A. Morsali, A.D. Hunter, M. Zeller, CrystEngComm. 9 (2007) 686.
- [12] G. Mahmoudi, A. Morsali, M. Zeller, Inorg. Chim. Acta 362 (2009) 217.
- [13] G. Mahmoudi, A. Morsali, M. Zeller, Solid State Sci. 10 (2008) 283.
- [14] G. Mahmoudi, A. Morsali, Cryst. Growth Des. 8 (2008) 391.
- [15] G. Mahmoudi, A. Morsali, Polyhedron 27 (2008) 1070.
- [16] A.D. Khalaji, G. Grivani, S. Jalali Akerdi, H. Stoeckli-Evan, D. Das, J. Chem. Crystallogr. 42 (2012) 83.
- [17] A.D. Khalaji, K. Fejfarova, M. Dusek, Russ. J. Coord. Chem. 37 (2011) 743.
- [18] A.D. Khalaji, S. Jalali Akerdi, G. Grivani, H. Stoeckli-Evan, D. Das, Russ. J. Coord. Chem. 37 (2011) 578.

- [19] A.D. Khalaji, G. Grivani, M. Rezaei, K. Fejfarova, M. Dusek, Polyhedron 30 (2011) 2790.
 [20] A.D. Khalaji, M. Weil, G. Grivani, S. Jalali Akerdi, Monatsh. Chem. 141 (2010)
- 539.
 [21] M. Khaledi, R. Kia, W. Clegg, R.W. Harrington, Acta Crystallogr., Sect. E 67 (2011) 03107.
- [22] M.C. Burla, M. Camalli, B. Carrozzini, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna, J. Appl. Crystallogr. 36 (2003) 1103.
 [23] V. Petricek, M. Dusek, L. Palatinus, JANA2006. Structure Determination Software
- Programs, Institute of Physics, Praha, Czech Republic, 2008.
- [24] L.J. Farrugia, J. Appl. Crystallogr. 30 (1997) 65.