# ORIGINAL PAPER

# Synthesis, Spectroscopic and Thermal Studies of Zinc(II) Complexes with the Symmetrical Bidentate Schiff-Base Ligand (2,3-MeO-ba)<sub>2</sub>en: Crystal Structure of Zn((2,3-MeO-ba)<sub>2</sub>en)I<sub>2</sub>

Aliakbar Dehno Khalaji · Gholamhossein Grivani · Samaneh Jalali Akerdi · Helen Stoeckli-Evans · Debasis Das

Received: 29 January 2011/Accepted: 17 November 2011/Published online: 1 December 2011 © Springer Science+Business Media, LLC 2011

Abstract Two zinc(II) complexes  $[ZnI_2((2,3-MeO-ba)_2en)]$ (1) and  $[ZnCl_2((2,3-MeO-ba)_2en)]$  (2), with the symmetrical bidentate Schiff-base ligand  $(2,3-MeO-ba)_2en$ [N,N'-bis(2,3-dimethoxybenzylidene)-1,2-diaminoethane] have been synthesized and characterized by elemental analyses (CHN), FT-IR and <sup>1</sup>H-NMR spectroscopy. The thermal behaviors of these complexes were studied using thermogravimetry in order to evaluate their thermal stability and thermal decomposition pathways. The crystal structure of  $[ZnI_2((2,3-MeO-ba)_2en)]$  (1) was determined from single-crystal X-ray diffraction. The coordination polyhedron about the zinc(II) center in the complex 1 is best described as a distorted tetrahedron.

**Keywords** Schiff-base; zinc(II) complexes · Spectroscopy; single-crystal · Thermal

A. D. Khalaji (⊠) Department of Chemistry, Faculty of Science, Golestan University, Gorgan, Iran e-mail: alidkhalaji@yahoo.com; ad.khalaji@gu.ac.ir

G. Grivani · S. J. Akerdi School of Chemistry, Damghan University, Damghan, P. O. Box 36715-364, Iran

H. Stoeckli-Evans Institute of Physics, University of Neuchâtel, Rue Emile-Argand 11, CH-2009 Neuchatel, Switzerland

## D. Das

Department of Chemistry, The University of Burdwan, Burdwan, West Bengal, India

### Introduction

The coordination chemistry of transition metals containing the bidentate Schiff-base ligands has been of interest for many years [1-5]. The preparation of new Schiff-base ligands is perhaps the interesting step in the development of coordination chemistry of transition metals [6-10]. These ligands have played a special role as chelating ligands in transition metal complexes due to their stability [1-10]. These complexes are an important class of coordination chemistry not only because they have interesting properties and geometry, but also they have found important applications in catalysis [11, 12].

Although the coordination chemistry of symmetric bidentate Schiff-base ligands with copper(I) has been extensively studied [6–12], there is few data on zinc(II) complexes with these ligands [13–17]. In a continuation of our work on the preparation of zinc(II) complexes with bidentate Schiff-base ligands [18–20], here we report the synthesis and characterization of two zinc(II) complexes [ZnI<sub>2</sub>((2,3-MeO-ba)<sub>2</sub>en)] (1) and [ZnCl<sub>2</sub>((2,3-MeO-ba)<sub>2</sub>en)] (2), with the symmetrical bidentate Schiff-base ligand (2,3-MeO-ba)<sub>2</sub>en [N,N'-bis(2,3-dimethoxybenzylidene)-1,2-diaminoethane] (Scheme 1).

# Experimental

Materials and General Methods

All reagents and solvents for synthesis and analysis were commercially available and used as received without further 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, and results agreed with calculated values. <sup>1</sup>H-NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz for the Schiff-base ligands and their complexes. All chemical shifts are reported in  $\delta$  units downfield from TMS. Thermogravimetric analyses were done on a Perkin Elmer TGA/DTA lab system 1 (Technology by SII) in nitrogen atmosphere with a heating rate of 20 °C/min from 35–700 °C.

# Preparation of (2,3-MeO-ba)<sub>2</sub>en Ligand

solution of 2,3-dimethoxybenzaldehyde (3.30 g, Α 0.02 mol) in 25 mL methanol was heated and stirred for 15 min. To this stirring solution, a solution of ethylenediamine (0.6 g, 0.01 mol) in 15 mL methanol was added dropwise with constant stirring. The mixture was heated at about 50 °C for 1.5 hours and then allowed to cool overnight at 273 K. The resulting crude solid was collected by filtration and dried at room temperature. Crystals were grown by the slow evaporation technique at room temperature in 25 mL methanol as a solvent for 5 days. At the period of super saturation, tiny crystals were nucleated. They were allowed to grow to a maximum possible dimension and then filtered. Yield: 3.28 g, 92%. Colorless crystals. Anal. Calc. for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>: C, 67.39; H, 6.78; N, 7.86%. Found: C, 67.35; H, 6.69; N, 7.79%. IR (KBr pellet,  $cm^{-1}$ ): 2,830 (s, CH=N), 2,842-3,010 (m, C-H aromatic and aliphatic), 1,654 (s, C=N), 1595, 1496, 1460, 1416 (s, C=C aromatic). <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ (ppm)): 3.76 (s, 6H), 3.84 (s, 6H), 3.99 (s, 4**H**), 6.91 (dd, 2**H**), 7.02 (t, j = 7.95, 2**H**), 7.51 (dd, 2H), 8.64 (s, 2H).

# Preparation of $[ZnI_2((2,3-MeO-ba)_2en)]$ (1)

To a stirring solution of the  $(2,3-MeO-ba)_2$ en ligand (0.071 g, 0.2 mmol), in 5 mL chloroform) was added ZnI<sub>2</sub> (0.064 g, 0.2 mmol) in 10 mL methanol and the mixture

**Table 1** Crystallographic data and structure refinement for  $[ZnI_2((2,3-MeO-ba)_{2}en)]$  (1)

| Empirical formula   | $C_{20}H_{24}N_2O_4ZnI_2$  |
|---|----------------------------|
| Formula weight  | 675.58                     |
| Crystal system, space group   | Monoclinic, C2/c           |
| <i>T</i> (K)  | 173                        |
| a (Å)   | 29.384 (3) Å               |
| <i>b</i> (Å)  | 7.2220 (4) Å               |
| <i>c</i> (Å)  | 12.2890 (9) Å              |
| $\beta$ (deg)   | 113.724 (6)                |
| $V(\text{\AA}^3)$   | 2,387.5 (3) Å <sup>3</sup> |
| Ζ   | 4                          |
| $\mu (\mathrm{mm}^{-1})$  | $3.64 \text{ mm}^{-1}$     |
| $T_{\min}, T_{\max}$  | 0.098, 0.171               |
| Measured reflections  | 10554                      |
| Independent reflections   | 2262                       |
| Reflection with $I > 2\sigma(I)$  | 1775                       |
| R <sub>int</sub>  | 0.09                       |
| S   | 1.04                       |
| $R[F^2 > 2\sigma(F^2)]$   | 0.042                      |
| $wR(F^2)$   | 0.094                      |
| Parameters  | 135                        |
| $\Delta \rho_{\rm max},  \Delta \rho_{\rm min}  ({\rm e} {\rm \AA}^{-3})$ | 0.72, -0.60                |
| Crystal size (mm <sup>3</sup> )   | $0.03\times0.40\times0.45$ |

was stirred for 10 min in air at room temperature and was then left at 273 K for several days without disturbance. Single crystals suitable for X-ray crystallography of **1** were obtained by slow evaporation of solvent. They were filtered off and washed with Et<sub>2</sub>O. Yield: 0.12 g, 89%. Colorless crystals. *Anal.* Calc. for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>ZnI<sub>2</sub>: C, 35.55; H, 3.58; N, 4.15%. Found: C, 35.45; H, 3.36; N, 4.18%. IR (KBr pellet, cm<sup>-1</sup>): 2,833 (s, CH=N), 2,864–3,033 (m, C–H aromatic and aliphatic), 1651 (s, C=N), 1582, 1487, 1464, 1429 (s, C=C aromatic). <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ (ppm)): 3.64 (s, 6H), 3.78 (s, 6H), 3.87 (s, 4H), 7.02–7.09 (m, 4H), 7.37 (dd, 2H), 8.49 (s, 2H).







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

| 2.5454(6)  |
|------------|
| 2.069(5)   |
| 2.069(5)   |
| 1.391(7)   |
| 1.427(10)  |
| 1.363(8)   |
| 1.429(10)  |
| 1.476(8)   |
| 1.247(11)  |
|            |
| 108.62(14) |
| 120.61(3)  |
| 114.80(13) |
| 114.80(13) |
| 83.6(2)    |
| 108.62(14) |
| 115.7(5)   |
| 117.6(5)   |
| 108.0(5)   |
| 134.9(4)   |
| 116.0(5)   |
| 108.0(5)   |
| 124.9(5)   |
| 118.3(5)   |
| 119.9(6)   |
| 116.5(5)   |
| 125.5(6)   |
|            |

i: x, y, -z + 1/2

Table 3 Selected torsion angles (°) of 1

|                          | 100.000   |
|--------------------------|-----------|
| C2-N1-C1-C1 <sup>i</sup> | 128.8(6)  |
| C1-N1-C2-C3              | 178.4(5)  |
| N1-C2-C3-C8              | -33.8(9)  |
| N1-C2-C3-C4              | 149.5(6)  |
| C2-C3-C4-C5              | 178.0(6)  |
| C2–C3–C8–C7              | -177.6(6) |

i: -x, y, -z + 1/2

# Preparation of $[ZnCl_2((2,3-MeO-ba)_2en)]$ (2)

This complex was prepared by a procedure similar to **1** using 0.2 mmol (0.027 g) of ZnCl<sub>2</sub> dissolved in in 10 mL methanol. Yield: 0.074 g, 86%. Colorless crystals. *Anal.* Calc. for C<sub>20</sub>H<sub>24</sub>N<sub>2</sub>O<sub>4</sub>ZnCl<sub>2</sub>: C, 48.75; H, 4.91; N, 5.69%. Found: C, 48.48; H, 4.73; N, 5.67%. IR (KBr pellet, cm<sup>-1</sup>): 2,834 (s, CH=N), 2853–3039 (m, C–H aromatic and aliphatic), 1636

| Table 4 | Inter-molecular | hvdrogen | bond | geometry | for 1 |
|---------|-----------------|----------|------|----------|-------|

| D–H···A                    | D–H  | $H \cdots A$ | $D \cdots A$ | D−H…A |
|----------------------------|------|--------------|--------------|-------|
| C9–H9C····O2 <sup>ii</sup> | 0.98 | 2.57         | 3.438(10)    | 148   |
| C10–H10A…O1 <sup>iii</sup> | 0.98 | 2.53         | 3.472(10)    | 161   |

Symmetry codes: ii -x - 1/2, -y - 1/2, -z; iii -x - 1/2, y + 1/2, -z + 1/2

(s, C=N), 1583, 1483, 1458, 1444 (s, C=C aromatic). <sup>1</sup>H-NMR (CDCl<sub>3</sub>,  $\delta$ (ppm)): 3.64 (s, 6H), 3.78 (s, 6H), 3.87 (s, 4H), 7.02–7.09 (m, 4H), 7.38 (dd, 2H), 8.50 (s, 2H).

#### X-Ray Crystallography for 1

Single crystals suitable for X-ray crystallography of 1 was obtained as colorless plates by slow evaporation of solvent at 273 K {Crystal size:  $0.03 \times 0.40 \times 0.45 \text{ mm}^3$ }. The intensity data were collected at 173 K (-100 °C) on a Stoe Mark II-Image Plate Diffraction System [21] equipped with a two-circle goniometer and using MoKa graphite monochromated radiation ( $\lambda = 0.71073$  Å). Image plate distance 130 mm,  $\omega$  rotation scans 0–180° at  $\phi$ 0°, and 0–62.0° at  $\phi$ 90°, step  $\Delta \omega = 1.3^\circ$ , exposures of 7 min per image,  $2\theta$  range  $1.76-52.59^{\circ}, d_{\min} - d_{\max} = 2,3.107-0.802$  Å. The structure was solved by direct methods using the programme SHEL-XS-97 [22]. The refinement and all further calculations were carried out using SHELXL-97 [22]. The H-atoms were included in calculated positions and treated as riding atoms using SHELXL default parameters. The non-H atoms were refined anisotropically, using weighted full-matrix leastsquares on  $F^2$ . An empirical absorption correction was applied using the MULscanABS routine in PLATON [23]. The molecule has crystallographic  $C_2$  symmetry, with the zinc(II) atom sitting on the 2-fold rotation axis. Crystallographic data and details of the data collection and structure solution and refinements are listed in Table 1.

## **Results and Discussion**

## Synthesis

The Schiff-base N,N'-bis(2,3-dimethoxybenzylidene)-1,2diaminoethane, (2,3-MeO-ba)<sub>2</sub>en, was synthesized by the mixing of ethylenediamine and 2,3-dimethoxybenzaldehyde. The reaction of ZnX<sub>2</sub> and (2,3-MeO-ba)<sub>2</sub>en in methnol-chloroform solvent mixture at room temperature results in monomeric zinc(II) complexes as shown in Scheme 1. The Schiff-base ligand is soluble in a range of common organic solvents such as methanol, ethanol, chloroform, dichloromethane, acetone, acetonitrile, dimethylformamide and dimethylsulfoxide, but insoluble in water. The

**Fig. 3** Non-classical C–H···I and C–H···O hydrogen bonds in complex **1** (*dashed lines*)



complexes are only soluble in coordinate solvents such as dimethylformamide and dimethylsulfoxide, but insoluble in a range of common organic solvent such as methanol, ethanol, chloroform, dichloromethane, acetone, acetonitrile and water.

## Spectral Studies

The most characteristic absorptions of the bidentate Schiffbase ligand  $(2,3-\text{MeO-ba})_2\text{en}$  and its zinc(II) complexes are presented in the experimental section. The complexes exhibit ligand absorption at different frequencies indicating the coordination of the ligands [13–18]. The v(C=N) band which appears at 1,654 cm<sup>-1</sup> in the free ligand, (2,3-MeO-ba)\_2\text{en}, shift to lower frequency, 1,651 cm<sup>-1</sup> (1) and 1,636 cm<sup>-1</sup> (2), upon complexation [13–18].

The <sup>1</sup>H-NMR spectra of zinc(II) complexes were recorded using DMSO- $d_6$  are shown in Fig. 1a and b, respectively. The <sup>1</sup>H-NMR spectra of the Schiff-base and its zinc(II) complexes suggest that the ligand has symmetrical structure in free and in the complexes. The complexes exhibit similar signals to the free ligand, indicating the coordination of the ligand to the metal ions [13–18]. All methylene and methoxy protons appear as a singlet in the region 3.6–4.0 ppm. In the region of 6.60–7.65 ppm were assigned chemical schifts for hydrogen of symmetrical aromatic ring of ligands. The <sup>1</sup>H-NMR spectra of the Schiff-base ligands and their complexes show a singlet in the region 8.37–8.65 ppm, which has been assigned to the azomethine (HC=N) proton.

## Crystal and Molecular Structure of 1

The molecular structure of  $[ZnI_2(2,3-MeO-ba)_2en]$  (1) with the atom-numbering schemes is presented in Fig. 2. Selected bond distances and angles are given in Table 3.



Fig. 4 TG graph of 1 (a) and 2 (b)

Structure of **1**, show the zinc(II) is coordinated by the bidentate Schiff-base ligand  $(2,3-MeO-ba)_2en$  and two iodine ions. While a tetrahedral geometry might be expected for a four coordinated zinc(II) center, the geometry around the zinc(II) ion in **1** is distorted by the restricting bite of chelate angle N1–Zn1–N1<sup>i</sup> 83.60(2)°of the Schiff-base ligands. This angle is in the range of 82–89° found for ethylenediamine chelate compounds [13–18], and much less than 109.5°. On the contrary the I1–Zn1–I1<sup>i</sup> angle has opened up to 120.61(3)°. The N–Zn–I angles are also distorted from the tetrahedral values (Table 2).

The average Zn–N bond lengths of 2.069 Å and Zn–I bond lengths of 2.545 Å agree well with the same distances

in other tetrahedral zinc(II) complexes [19, 20]. The geometry about the zinc(II) center in these complexes is also approximately tetrahedral, with distortion indicated by the unequal metal–ligand bond distances and angles. In order to obtain a low structure preference energy for other complexes with  $d^{10}$  ions, then a distorted tetrahedral structure can be inferred for other zinc(II) complexes [13–20]. The Schiff-base ligand (2,3-MeO-ba)<sub>2</sub>en adopts a *Z*,*Z* configuration in this complex [18–20]. The value for the dihedral angles C1–N1–C2–C3 is 178.4(5)° and C2–C3–C8–C7 is –177.6(6)°, indicating an almost planar configuration of this moiety for the complexes studied here (Table 3) [18–20].

The geometry of hydrogen bonds in **1** is given in Table 4. Complex **1**, exhibits a different hydrogen bonding pattern built up from non-classical C–H…O hydrogen bonds in the crystal structure (Fig. 3).

## Thermal Analysis

Thermogravimetric analyses of these complexes under N<sub>2</sub> were examined and the TG graphs are shown in Fig. 4. The title compounds [ZnI<sub>2</sub>(2,3-MeO-ba)<sub>2</sub>en] (1) and [ZnCl<sub>2</sub>(2,3-MeO-ba)<sub>2</sub>en] (2) are stable up to 471 and 489 K, respectively, and during further heating undergoes decomposition in four stages. Complex 1 shows a weight loss of 19.89%  $(\approx 134.37 \text{ g})$  in the temperature range 471–492 K, corresponding to the removal of one (Ch<sub>3</sub>O)<sub>2</sub>Ph group (Calcd. 20.27%), 9.61% ( $\approx 64.92$  g) in the temperature range 492-626 K, corresponding to the removal of two methoxy groups (Calcd. 9.17%), 11.24% (~75.94 g) in the temperature range 626–774 K, corresponding to the removal of one Ph group (Calcd. 11.11%) and 19.84% ( $\approx$ 134.03 g) in the temperature range 774-1013 K, corresponding to the removal of one C and I groups (Calcd. 20.57%). While, complex 2 shows a weight loss of 9.82% ( $\approx$ 48.46 g) in the temperature range 489–515 K, corresponding to the removal of four methyl groups (Calcd. 12.17%), 13.24% ( $\approx 65.35$  g) in the temperature range 515-635 K, corresponding to the removal of four oxygen atoms (Calcd. 12.98%), 20.35%  $(\approx 100.44 \text{ g})$  in the temperature range 635–876 K, corresponding to the removal of one Ph–C group (Calcd. 17.86%) and 17.47% ( $\approx$ 86.23 g) in the temperature range 876-1013 K, corresponding to the removal of one Ph-C group (Calcd. 17.86%).

# Conclusion

We have synthesized tetrahedral Zn(II) complex with Schif base ligand (2,3-MeO-ba)<sub>2</sub>en. All compounds (ligand and the complexes) are well characterized by different spectroscopic techniques and microanalytical data. The structure of 1 has been confirmed by X-ray crystallographic analysis. Thermal stability and decomposition pattern of the Zn(II) complexes are described elaborately.

Acknowledgments We acknowledge Golestan University (GU) and Damghan University (DU) for partial support of this work, The University of Burdwan (UB) for TG and University of Neuchâtel (UN) for X-ray analysis.

## References

- 1. Drew MGB, De S, Datta D (2009) Inorg Chim Acta 362:2487
- Das S, Sarkar BN, Bhar K, Chattopadhyay S, Fun HK, Mitra P, Ghosh BK (2010) Inorg Chem Commun 13:353
- Dolaz M, McKee V, Urus S, Demir N, Sabik AE, Golcu A, Tumer N (2010) Spectrochim Acta A76:174
- Morshedi M, Amirnasr M, Triki S, Khalaji AD (2009) Inorg Chim Acta 362:1637
- Morshedi M, Amirnasr M, Slawin AMZ, Woollins JD, Khalaji AD (2009) Polyhedron 28:167
- 6. Pascu M, Clarkson GJ, Kariuki BM, Hannon MJ (2006) Dalton Trans 22:2635
- 7. Price JR, Lan Y, Brooker S (2007) Dalton Trans 18:1807
- 8. Zhou XH, Wu T, Li D (2006) Inorg Chim Acta 359:1442
- 9. Zhang G, Yang G, Ma JS (2006) J Chem Crystallogr 36:631
- Dehghanpour S, Mahmoudi A, Hadjikhani R (2008) J Braz Chem Soc 19:600
- Ardizzoia GA, Brenna S, Castelli F, Galli S (2009) Inorg Chim Acta 362:3507
- Sawant SK, Gaikwad GA, Sawant VA, Yamgar BA, Chavan SS (2009) Inorg Chem Commun 12:632
- Dehghanpour S, Mahmoudi A (2007) Synth React Inorg Met-Org Nano-Met Chem 37:35
- Montazerozohori M, Joohari S, Musavi SA (2009) J Coord Chem 62:1285
- 15. Montazerozohori M, Musavi SA (2008) J Coord Chem 61:3934
- Marjani K, Asgarian J, Mousavi M, Amani V (2009) Z Anorg Allg Chem 635:1633
- Prakash A, Singh BK, Bhojak N, Adhikari D (2010) Spectrochim Acta A76:356
- Khalaji AD, Weil M, Grivani G, Jalali Akerdi S (2010) Mon Chem 141:539
- 19. Khalaji AD, Zhang Y, Mojdekanlou S (2008) Anal Sci 24:x131
- 20. Khalaji AD, Jian F, Xiao H, Mojdekanlou S (2008) Anal Sci 24:x91
- Stoe Cie (2009) X-Area V1.52 & X-RED32 V1.48 Software. Stoe & Cie GmbH, Darmstadt
- 22. Sheldrick GM (2008) Acta Cryst A64:112
- 23. Spek AL (2009) Acta Cryst D65:148