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ORIGINAL PAPER

Synthesis, characterization, and crystal structure of two zinc(II) halide complexes with the symmetrical bidentate Schiff-base ligand (3,4-MeO-ba)$_2$en

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Abstract In this study two zinc(II) halide complexes with the Schiff-base ligand (3,4-MeO-ba)$_2$en [*N*,*N*′-bis(3,4-dimethoxybenzylidene)ethane-1,2-diamine] have been synthesized and characterized by elemental analyses (CHN), single-crystal X-ray diffraction, Fourier-transform infrared (FT-IR), and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. The metal-to-ligand ratio was found to be 1:1 within the formula ZnX$_2$((3,4-MeO-ba)$_2$en) (X = Br, I). Crystal structure analysis reveals that the coordination geometry around the zinc(II) ions in the two isotypic complexes is distorted tetrahedral. The Schiff-base ligand (3,4-MeO-ba)$_2$en acts as a chelating ligand and coordinates via two N atoms to the metal center and adopts an (*E*,*E*) conformation. The coordination spheres of the metal atoms are completed by the two halide atoms, which are also involved in weak non-classical hydrogen-bonding interactions of the type C–H···X–Zn.

Keywords Zinc(II) complexes · Schiff base · Crystallography · Tetrahedral coordination

Introduction

Schiff-base compounds are typically formed by condensation of a primary amine and an aldehyde [1, 2]; they are used as substrates in the preparation of a number of transition-metal complexes [3–5]. They have good catalysis ability [6, 7] and are suitable for generation of supramolecular structures [8, 9]. The coordination behavior of Schiff-base ligands depends on the metal ion, the reaction conditions, and the nature of the anion and the solvent used [10–15]. Transition-metal complexes with neutral bidentate Schiff-base compounds as ligands have played an important role in the development of coordination chemistry [16–20].

Zinc(II) complexes with Schiff-base ligands have been investigated particularly for their catalytic activities [21] and as potential luminescent materials [22]. Recent works have focused on synthesis of new Schiff-base ligands containing the diimine chelating function [23]. As an additional contribution to the synthesis, characterization, and crystal structures of zinc(II) Schiff-base complexes and in the course of our ongoing studies of these kinds of materials [24, 25], we describe herein the synthesis, characterization, and crystal structures of two Zn(II) complexes [ZnX$_2$((3,4-MeO-ba)$_2$en), X = Br (**1**), I (**2**)] (Scheme 1).

Results and discussion

Synthesis and characterization

(3,4-MeO-ba)$_2$en was prepared by condensation of 3,4-dimethoxybenzaldehyde with ethylenediamine following literature methods [26, 27]. The Schiff-base ligand (3,4-MeO-ba)$_2$en is soluble in common solvents such as CHCl$_3$ and CH$_2$Cl$_2$, while the respective Zn complexes are soluble

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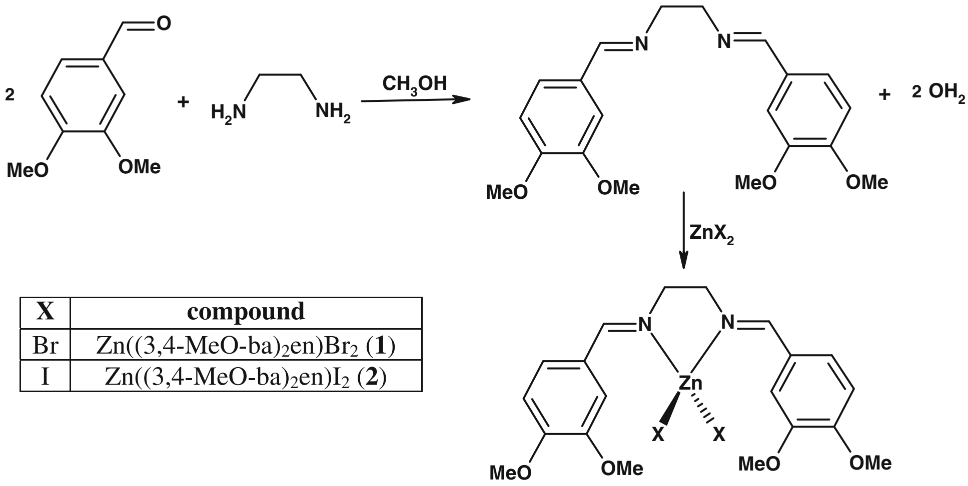
Scheme 1



X	compound
Br	Zn((3,4-MeO-ba)$_2$en)Br$_2$ (**1**)
I	Zn((3,4-MeO-ba)$_2$en)I$_2$ (**2**)

in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO), but insoluble in EtOH, MeOH, $CHCl_3$, and CH_2Cl_2. All compounds synthesized in this work are stable at room temperature in the solid state. The stability of dissolved complexes depends on the nature of the solvent. They are stable in coordinating solvents such as DMF and DMSO at room temperature for about 10 days, and at 273 K for about 20 days.

Infrared spectra

The IR spectra of the free ligand (3,4-MeO-ba)$_2$en exhibit the characteristic band of the imine group (–C=N–), which appears at 1636 cm^{-1} [26, 27]. This band is shifted in the complexes toward lower frequencies because of the coordination of the nitrogen atom to the metal ion [28], and appears at 1625 cm^{-1} (**1**) and at 1623 cm^{-1} (**2**). The observed red-shift of the –C=N– vibration with an addition coordination to the Zn atom can be attributed to the metal-to-ligand π-back bonding. The ligand's stretching vibrations at about 2820–3050 cm^{-1}, assigned to C–H iminic, aromatic, and aliphatic groups, are shifted to lower energy after coordination to metal ions [28]. In the infrared spectra of the complexes, the bands in the range 450–490 cm^{-1} that are absent in the spectrum of the pure ligand may be due to vibrational modes of Zn–N bonds, supporting the coordination of two iminic nitrogen atoms [28].

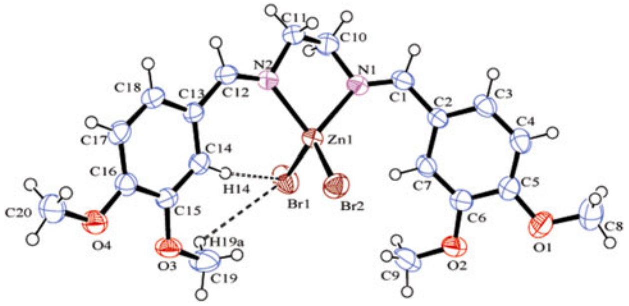


Fig. 1 Molecular structure of **1**, showing 50% probability displacement ellipsoids and atom numbering. *Dashed lines* indicate nonclassical C–H···Br hydrogen bonds

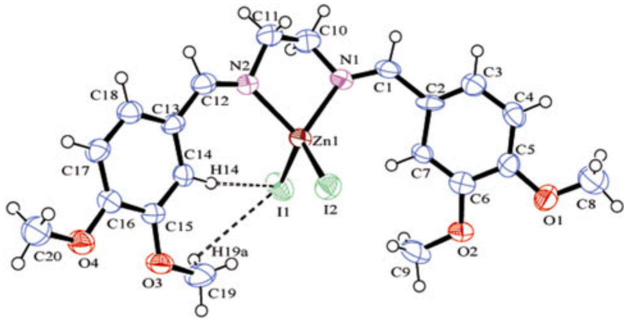


Fig. 2 Molecular structure of **2**, showing 50% probability displacement ellipsoids and the atom numbering. *Dashed lines* indicate nonclassical C–H···I hydrogen bonds

^{1}H NMR spectra

The Schiff-base ligand (3,4-MeO-ba)$_2$en has symmetric nature, therefore the hydrogen atoms in the two halves of the –CH$_2$–CH$_2$– fragment are equivalent. The azomethine groups show up at $\delta = 8.16$ ppm as a single signal [26, 27]. In the complexes, the signals related to this group are shifted to lower regions [8.30 ppm (**1**) and 8.22 ppm (**2**)]. This shift shows that the nitrogen atom of the –CH=N– group is coordinated to zinc(II) ions [29, 30]. Signals of aromatic ring protons of the (3,4-MeO-ba)$_2$en fragment appear in the range 6.75–7.50 ppm and are also shifted to the lower regions in the complexes. In the free ligand, signals of hydrogen atoms of the methoxy groups and

Table 1 Selected bond distances and angles for **1** and **2**

	1	**2**
Zn(1)-N(1) (Å)	2.062 (2)	2.066 (5)
Zn(1)-N(2) (Å)	2.087 (2)	2.084 (5)
Zn(1)-X(1) (Å)	2.3550 (6)	2.5475 (8)
Zn(1)-X(2) (Å)	2.3571 (8)	2.5502 (8)
N(1)-C(1) (Å)	1.275 (3)	1.295 (7)
N(1)-C(10) (Å)	1.468 (3)	1.459 (8)
N(2)-C(12) (Å)	1.284 (3)	1.276 (8)
N(2)-C(11) (Å)	1.477 (3)	1.478 (8)
N(1)-Zn(1)-N(2) (°)	83.74 (9)	83.73 (19)
N(1)-Zn(1)-X(1) (°)	107.46 (7)	107.74 (15)
N(2)-Zn(1)-X(1) (°)	113.01 (6)	112.56 (15)
N(1)-Zn(1)-X(2) (°)	118.96 (6)	118.26 (15)
N(2)-Zn(1)-X(2) (°)	111.68 (7)	112.01 (15)
X(1)-Zn(1)-X(2) (°)	117.37 (3)	117.75 (3)
C(1)-N(1)-C(10) (°)	119.3 (2)	118.8 (5)
C(1)-N(1)-Zn(1) (°)	133.67 (19)	134.6 (4)
C(10)-N(1)-Zn(1) (°)	106.00 (16)	105.8 (4)
C(12)-N(2)-C(11) (°)	115.9 (2)	115.5 (5)
C(12)-N(2)-Zn(1) (°)	135.30 (18)	135.4 (4)
C(11)-N(2)-Zn(1) (°)	108.34 (16)	108.4 (4)

Table 2 Intra- and intermolecular hydrogen-bond geometry for **1**

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
C(14)-H(14)···Br(1)	0.93	3.122	3.999 (3)	158
C(19)-H(19A)···Br(1)	0.96	3.358	3.961 (3)	123
C(10)-H(10B)···O(3)[a]	0.97	2.56	3.521 (4)	170
C(19)-H(19B)···O(1)[b]	0.96	2.57	3.514 (4)	168

[a] $1 + x, 1 + y, z$

[b] $-x, 1 - y, 1 - z$

Table 3 Intra- and intermolecular hydrogen-bond geometry for **2**

D-H···A	D-H (Å)	H···A (Å)	D···A (Å)	D-H···A (°)
C(14)-H(14)···I(1)	0.93	3.297	4.176 (8)	158
C(19)-H(19A)···I(1)	0.96	3.539	4.134 (8)	122
C(19)-H(19B)···O(1)[a]	0.96	2.56	3.493 (9)	163

[a] $-x, 1 - y, 1 - z$

ethylenediamine are observed in the 3.70–4.00 ppm region [26, 27], and are likewise shifted to lower regions after coordination [29, 30].

Description of the crystal structures of 1 and 2

The molecular structures of the complexes **1** and **2**, including the atom-numbering schemes, are illustrated in Figs. 1 and 2, respectively, and selected bond lengths and angles are given in Table 1. The zinc(II) ions in **1** and **2** are tetrahedrally coordinated by two nitrogen atoms from the Schiff-base ligand (3,4-MeO-ba)$_2$en and by two halogen atoms. The coordination about the Zn(II) ions is considerably distorted due to the restricting bite angles of the chelating ligands. The N(1)–Zn(1)–N(2) angle is only 83.74(9)° in **1** and 83.73(19)° in **2**, being in the same range of 82(3)°–90(3)° found for ethylenediamine-chelated Zn(II) complexes [24, 25, 31]. The Br(1)–Zn(1)–Br(2) angle is 117.37(3)° in **1** and I(1)–Zn(1)–I(2) is 117.75(3)° in **2**. The deviation from a regular tetrahedral angle (109.5°) is due to the steric effects from the bulky bromo and iodo groups. The other bond angles, N–Zn–Br in **1** and N–Zn–I in **2**, are also indicative of large deviation from the idealized tetrahedral symmetry. These angles are similar to those found in [ZnCl$_2$(Phca)$_2$en] [31], [ZnBr$_2$(3,4,5-MeO-ba)$_2$en] [24], and [ZnI$_2$(3,4,5-MeO-ba)$_2$en] [25]. The average Zn–N bond lengths of 2.074 Å in **1** and 2.075 Å in **2** and the Zn–X bond lengths of 2.356 Å in **1** and 2.548 Å in **2** agree well with corresponding bond lengths in other complexes with tetrahedrally coordinated zinc(II) atoms [24, 25, 31]. The ligand (3,4-MeO-ba)$_2$en adopts an (*E*,*E*) configuration in these complexes [24, 25, 31]. The values for the dihedral angles C(10)–N(1)–C(1)–C(2) and C(11)–N(2)–C(12)–C(13) are 175.4(2)° and 176.1(2)° in **1** and 175.0(6)° and 173.5(6)° in **2**, indicating an almost planar configuration of this moiety for the complexes studied here. There are similar non-classical hydrogen bonds of type

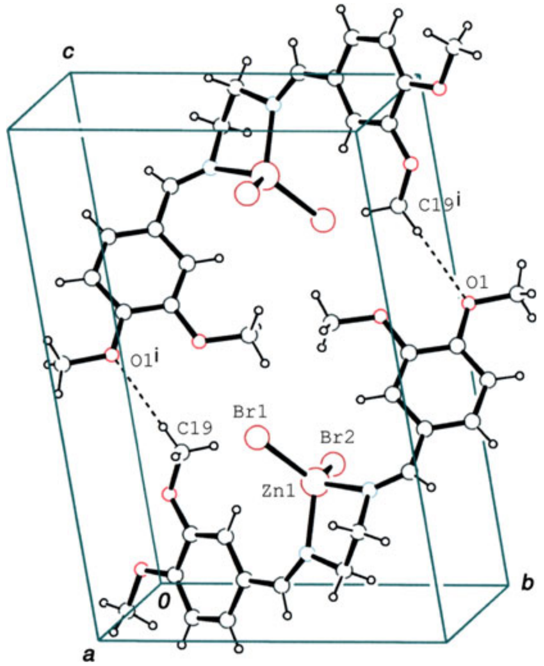


Fig. 3 Non-classical C–H···O hydrogen bonds in complex **1** (*dashed lines*)

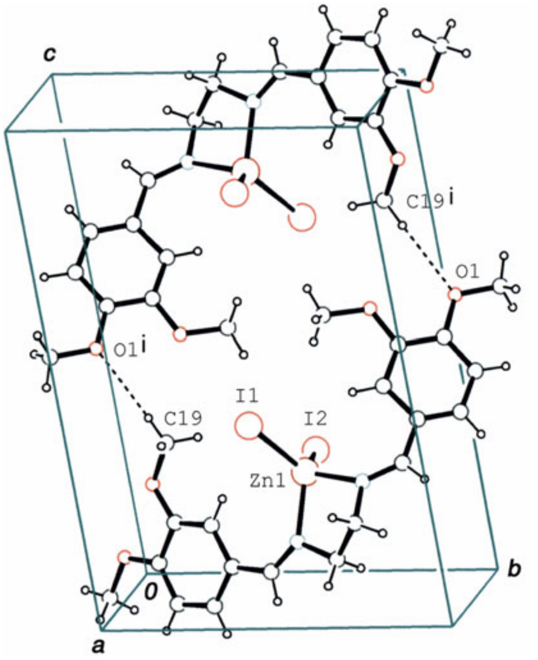


Fig. 4 Non-classical C–H···O hydrogen bonds in complex **2** (*dashed lines*)

C(14)–H(14)···X(1)–Zn and C(19)–H(19A)···X(1)–Zn in the crystal of **1** and **2** (Tables 2, 3; Figs. 1, 2). These intramolecular hydrogen bonds are formed between aromatic and methyl H-atoms of the bidentate Schiff-base ligand and the coordinated halogen atom. The [ZnX$_2$((3,4-MeO-ba)$_2$en)] molecules are eventually linked together via other non-classical C–H···O hydrogen bonds (Figs. 3, 4; Tables 2, 3).

Experimental

Materials and characterization

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 PerkinElmer spectrophotometer. Elemental analyses were carried out using a Heraeus CHN–O-Rapid analyzer, and results agreed with calculated values. ^{1}H NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz for the Schiff-base ligand and on a BRUKER DRX-400 AVANCE spectrometer at 400 MHz for zinc(II) complexes. All chemical shifts are reported in δ units downfield from tetramethyl silane (TMS). (3,4-MeO-ba)$_2$en was synthesized according to Refs. [26, 27], and measured analytical data were in agreement with values reported there.

Table 4 Crystallographic and refinement data for **1** and **2**

	1	**2**
Empirical formula	$C_{20}H_{24}Br_2N_2O_4Zn$	$C_{20}H_{24}I_2N_2O_4Zn$
Formula weight	581.60	675.58
Crystal system, space group	Triclinic, $P\,\bar{1}$	Triclinic, $P\,\bar{1}$
a (Å)	8.2334 (16)	8.1860 (10)
b (Å)	10.014 (2)	10.4659 (13)
c (Å)	14.920 (3)	14.9302 (17)
α (°)	99.84 (3)	99.725 (5)
β (°)	101.35 (3)	99.572 (5)
γ (°)	106.54 (3)	107.444 (5)
V (Å^3)	1122.0 (4)	1170.3 (2)
Z	2	2
D_x (g/cm^3)	1.722	1.917
μ (mm^{-1})	4.68	3.71
T_{min}, T_{max}	0.250, 0.603	0.187, 0.569
Measured reflections	29520	20286
Independent reflections	6463	4516
Reflection with $I > 2\sigma(I)$	4429	3457
Parameters	266	266
R_{int}	0.038	0.046
S	1.01	1.03
$R[F^2 > 2\sigma(F^2)]$	0.035	0.051
$wR(F^2)$	0.090	0.141
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (eÅ^{-3})	0.78, −0.32	2.95, −0.67

General procedure for synthesis of the zinc(II) complexes

The Zn(II) complexes were synthesized by addition of the (3,4-MeO-ba)$_2$en ligand (0.2 mmol, in 5 cm^3 chloroform) to a solution of the anhydrous metal salts (ZnX$_2$, 0.2 mmol, 10 cm^3 methanol, **1**: X = Br, **2**: X = I). The resulting solution was stirred in air at room temperature for about 2 h and was then left at 273 K for several days without disturbance, yielding single crystals of the complexes that subsequently were filtered off and washed with Et$_2$O.

Dibromo[N,N′-bis[(3,4-dimethoxyphenyl)methyl]-1,2-ethanediamine-κN, κN′]zinc (**1**, $C_{20}H_{24}Br_2N_2O_4Zn$)
Light yellow crystals. Yield: 75%. IR (KBr): $\bar{\nu}$ = 2837 (–HC=N–), 2917–2966 (C–H aliphatic), 2999 (C–H aromatic), 1625 (s, C=N), 1472–1596 (C=C aromatic) cm^{-1}; ^{1}H NMR (DMSO-d_6): δ = 3.77 (s, 16H, 2 CH$_3$–O– and –CH$_2$–CH$_2$–), 6.97 (d, 2H), 7.21 (dd, 2H), 7.40 (d, 2H), 8.30 (s, 2H, –CH=N–) ppm.

Diiodo[N,N′-bis[(3,4-dimethoxyphenyl)methyl]-1,2-ethanediamine-κN, κN′]zinc (**2**, $C_{20}H_{24}I_2N_2O_4Zn$)
Yellow crystals. Yield: 79%. IR (KBr): $\bar{\nu}$ = 2835 (–HC=N–), 2915–2963 (C–H aliphatic), 3004 (C–H aromatic), 1623 (s, C=N), 1469–1594 (C=C aromatic) cm^{-1}; ^{1}H

NMR (DMSO-d_6): $\delta = 3.74$ (s, 6H, CH_3–O–), 3.76 (s, 6H, CH_3–O–), 3.78 (s, 4H, –CH_2–CH_2–), 6.96 (dd, 2H), 7.18 (dd, 2H), 7.31 (d, 2H), 8.22 (s, 2H, –CH=N–) ppm.

Single-crystal X-ray analysis

Single crystals of **1** with dimensions $0.41 \times 0.18 \times 0.12$ mm^3 and **2** with dimensions $0.28 \times 0.20 \times 0.16$ mm^3 were chosen for X-ray diffraction studies. Intensity data collections were performed with Mo K_α radiation ($\lambda = 0.71073$ Å) at room temperature on an APEXII four-circle CCD diffractometer (Bruker AXS). Intensity data were corrected for absorption effects using the multi-scan approach with the program SADABS [32]. The crystal structures were solved by direct methods with the SHELXTL program suite [33] and were subsequently refined by full-matrix least-squares technique on F^2. H atoms were positioned geometrically (C–H distance = 0.93 or 0.96 Å) and were refined as riding, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$ or $1.5U_{\mathrm{eq}}$(methyl C), allowing for free rotation of the methyl groups. For structure **2** the highest remaining electron density peak and the deepest hole are located 1.04 Å from atom C20 and 0.80 Å from atom Zn1, respectively. Structure data and details of the data collections and structure refinements are listed in Table 4. The molecular structure plots were prepared by ORTEP III for Windows [34].

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 759100 (**1**) and 759099 (**2**). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk.

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