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Synthesis, Spectral Characterization, and Crystal Structure of Mononuclear Mercury(II) Complex [Hg((3,4-MeO-Bza)$_2$En)I$_2$][1]

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Abstract—Mercury(II) complex, [Hg((3,4-MeO-Bza)$_2$En)I$_2$] (**I**), where (3,4-MeO-Bza)$_2$En = N,N'-bis(3,4-dimethoxybenzaldehyde)ethylenediimine, has been synthesized from the reaction of HgI$_2$ with (3,4-MeO-Bza)$_2$En in methanol as solvent at 50°C. It was characterized by elemental analysis (CHN), ^{1}H-NMR spectroscopy and confirmed by single-crystal X-ray diffraction analysis. The complex **I** crystallizes in the monoclinic system, with space group $P2_1/c$, having one symmetry-independent Hg^{2+} ion coordinated in a distorted tetrahedral geometry by two N atoms of the Schiff base ligand and by two I atoms. The Schiff base ligand (3,4-MeO-Bza)$_2$En acts as a chelating ligand and coordinates via two N atoms to the mercury center. It adopts an (*E*, *E*) conformation.

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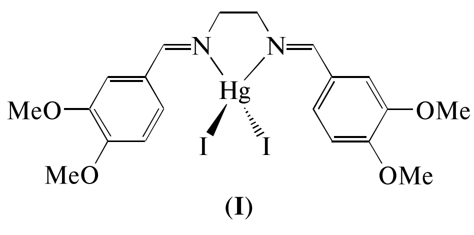
INTRODUCTION

The coordination chemistry of transition metal complexes, such as Cd(II) [1, 2], Ag(I) [3, 4], Pb(II) [5], Cu(I) [6], and Hg(II) [7–11] with N donor Schiff base ligands has been of special interest in recent years, because d^{10} configuration of transition metals may give rise to different coordination numbers and molecular and crystal structures. These complexes play an important role in the development of coordination chemistry related to molecular architectures [1–11]. Although many MLX$_2$ complexes of transition metals with bidentate diimine Schiff base ligands have been already investigated [12–15], mercury(II) complexes with Schiff base ligands remain rare [16, 17]. In a continuation of our work on d^{10} complexes with bidenate Schiff base ligands [18–20], herein we describe a new mononuclear mercury(II) complex, [Hg((3,4-MeO-Bza)$_2$En)I$_2$] (**I**):



(I)

EXPERIMENTAL

All reagents and solvents for synthesis and analysis were commercially available and used as received without further purifications. 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 ligands and their complexes. All chemical shifts are reported in δ units downfield from TMS. The bidenate Schiff base ligand (3,4-MeO-Bza)$_2$En was prepared following the standard procedure [4].

Synthesis of I. To a stirring solution of the (3,4-MeO-Bza)$_2$En ligand (0.2 mmol, in 5 mL of chloroform) was added HgI$_2$ (0.2 mmol) in 10 mL of methanol and the mixture was stirred for 10 min in air at room temperature. It was then left at 273 K for several days without disturbance yielding suitable crystals of **I** that subsequently were filtered off and washed with Et$_2$O. The yield was 79%.

For $C_{20}H_{24}N_2O_4I_2Hg$

anal. calcd., %:	C, 29.62;	H, 2.98;	N, 3.45.
Found, %:	C, 29.69;	H, 2.96;	N, 3.40.

^{1}H NMR (CDCl$_3$; δ, ppm): 3.79 (s., 6H), 3.80 (s., 6H), 3.83 (s., 4H), 7.02 (d., 2H), 7.26 (d., 2H), 7.41 (s., 2H), 8.40 (s., 2H).

X-ray structure determination. A single crystal of compound **I** with the dimensions 0.24 × 0.17 × 0.07 mm was chosen for X-ray diffraction study. Crystallo-

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Table 1. Crystallographic data and experimental details for complex **I**

Parameter	Value
Formula weight	810.8
Crystal system	Monoclinic
Space group	$P2_1/n$
T, K	120
a, Å	8.09390(10)
b, Å	22.0954(3)
c, Å	13.0968(2)
β, deg	96.6270(2)
V, Å^3	2326.56(6)
Z	4
μ, mm^{-1}	9.3
Measured reflections	32588
Independent reflections	4752
Reflections with $I > 2\sigma(I)$	4160
R_{int}	0.028
S	1.12
R ($F^2 > 2\sigma(F^2)$)	0.016
wR (F^2)	0.039
$\Delta\rho_{\min}/\Delta\rho_{\max}$, e Å^{-3}	−0.40/0.56

Table 2. Bond distances (Å) and bond angles (deg) for **I**

Bond	d, Å	Bond	d, Å
Hg(1)–I(1)	2.6867(2)	Hg(1)–N(1)	2.355(2)
Hg(1)–I(20)	2.6667(2)	Hg(1)–N(2)	2.396(2)
O(1)–C(5)	1.375(3)	O(3)–C(15)	1.361(3)
O(1)–C(9)	1.432(3)	O(3)–C(19)	1.429(3)
O(2)–C(6)	1.357(3)	O(4)–C(16)	1.353(3)
O(2)–C(10)	1.438(3)	O(4)–C(20)	1.434(3)
N(1)–C(10)	1.469(4)	N(2)–C(11)	1.475(4)
N(1)–C(2)	1.278(3)	N(2)–C(12)	1.280(3)
C(1)–C(11)	1.521(4)	C(12)–C(13)	1.456(4)
C(14)–C(15)	1.373(4)	C(13)–C(14)	1.405(4)
C(2)–C(3)	1.451(4)	C(13)–C(18)	1.393(4)
C(3)–C(4)	1.405(4)	C(15)–C(16)	1.414(4)
C(3)–C(8)	1.380(4)	C(16)–C(17)	1.382(4)
C(4)–C(5)	1.371(4)	C(17)–C(18)	1.391(4)
C(6)–C(7)	1.389(4)	C(5)–C(6)	1.408(4)
C(7)–C(8)	1.382(4)		
Angle	**ω, deg**	**Angle**	**ω, deg**
I(1)Hg(1)I(2)	124.991(7)	I(2)Hg(1)N(1)	120.33(5)
I(1)Hg(1)N(1)	104.15(5)	I(2)Hg(1)N(2)	110.53(6)
I(1)Hg(1)N(2)	111.08(5)	N(1)Hg(1)N(2)	74.83(7)
C(5)O(1)C(9)	116.5(2)	C(6)O(2)C(10)	116.4(2)
C(15)O(3)C(19)	116.6(2)	C(16)O(4)C(20)	117.7(2)
Hg(1)N(1)C(1)	107.74(15)	Hg(1)N(1)C(2)	133.2(2)
Hg(1)N(2)C(12)	133.3(2)	Hg(1)N(2)C(11)	109.15(15)
C(1)N(1)C(2)	118.4(2)	C(11)N(2)C(12)	116.5(2)
N(1)C(2)C(3)	125.2(3)	N(1)C(1)C(11)	109.1(2)
N(2)C(12)C(13)	127.3(3)	N(2)C(11)C(1)	111.2(2)
C(12)C(13)C(14)	123.7(2)	C(12)C(13)C(18)	116.7(2)
C(13)C(18)C(17)	120.1(3)	C(13)C(14)C(15)	120.2(2)
C(14)C(15)C(16)	120.1(2)	C(14)C(13)C(18)	119.5(3)
O(3)C(15)C(14)	125.4(2)	O(3)C(15)C(16)	114.5(2)
O(4)C(16)C(15)	115.3(2)	O(4)C(16)C(17)	125.2(2)
C(2)C(3)C(4)	122.2(2)	C(2)C(3)C(8)	119.3(2)
C(3)C(4)C(5)	120.8(2)	C(4)C(3)C(8)	118.5(3)
C(15)C(16)C(17)	119.5(2)	C(16)C(17)C(18)	120.5(2)
O(1)C(5)C(4)	124.5(2)	O(1)C(5)C(6)	115.6(2)
C(4)C(5)C(6)	119.8(2)	C(3)C(8)C(7)	121.5(3)
O(2)C(6)C(5)	116.2(2)	O(2)C(6)C(7)	124.4(2)
C(5)C(6)C(7)	119.5(2)	C(6)C(7)C(8)	119.8(2)

graphic measurements were done at 120 K with four-circle CCD diffractometer (Gemini of Oxford diffraction, Ltd.), using MoK_α radiation (λ = 0.71073 Å, graphite monochromator and area detector Atlas). The crystal structures were solved by direct methods with the SIR2002 program [21] and refined with the Jana2006 program package [22] by the full-matrix least-squares technique on F^2. The molecular structure plots were prepared by ORTEP III for Windows [23]. Hydrogen atoms were mostly discernible in difference Fourier maps and could be refined to reasonable geometry. According to common practice, they were nevertheless kept in ideal positions during the refinement, allowing only rotation of methyl groups. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as $1.2U_{\text{eq}}$ of the parent atom. Crystallographic data and details of the data collection and structure refinements are summarized in Table 1. Bond distances and angles are listed in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 829406; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The ligand (3,4-MeO-Bza)$_2$En was prepared under mild conditions. It reacted with HgI$_2$ (molar ratio 1 : 1) in a mixture of methanol–chloroform (2 : 1 v/v) at 298 K

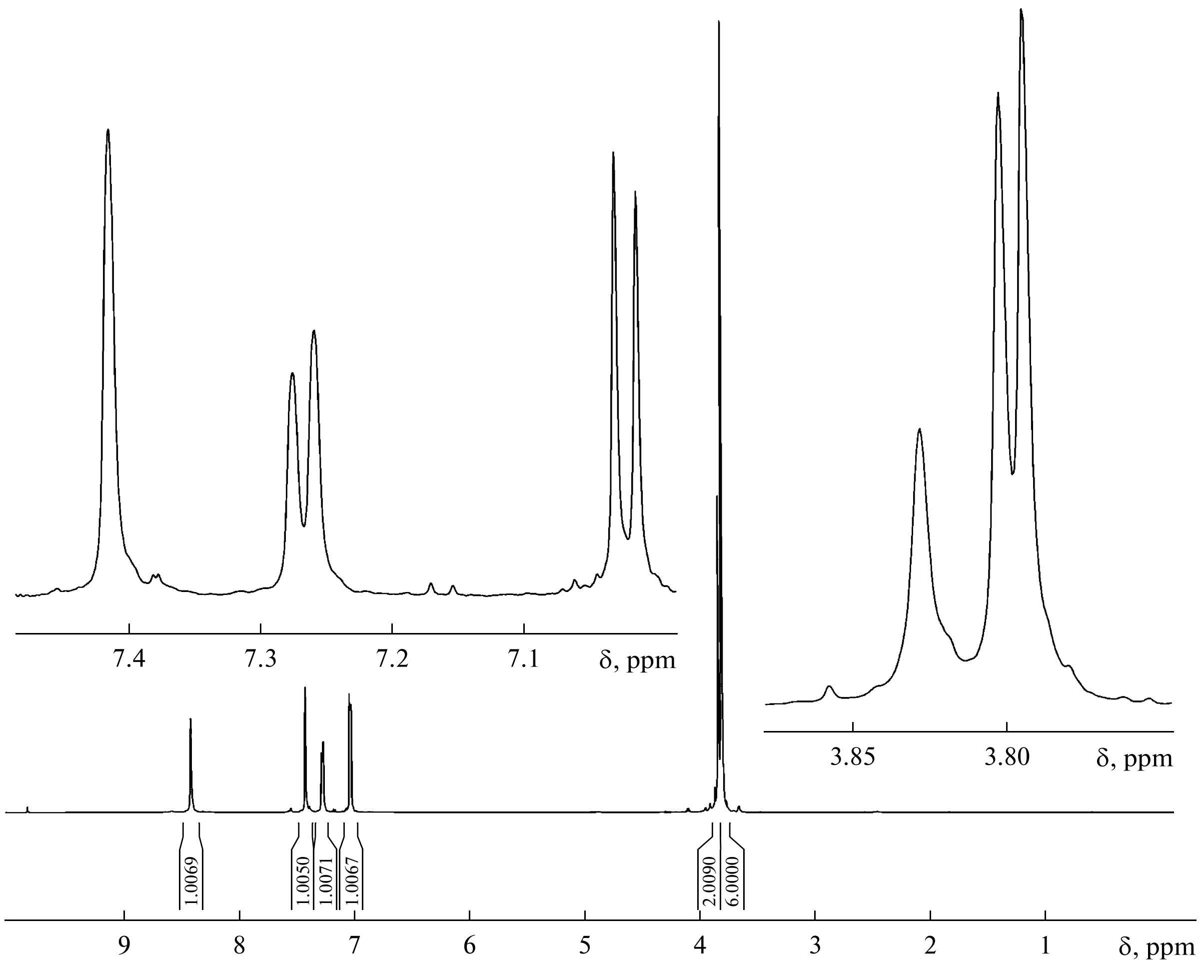

Fig. 1. ^{1}H NMR spectra of **I**.

to afford the corresponding mercury(II) complex **I** in 79% yield.

^{1}H NMR spectra of the complex recorded using $CDCl_3$ are summarized in the experimental section and shown in Fig. 1. The ^{1}H NMR spectra of **I** suggest that the ligand has a symmetrical structure in the complex. Methylene (CH_2–CH_2) protons appear as a singlet peak at 3.83 ppm, while methoxy (CH_3O–) protons appear as two singlet signals at 3.79 and 3.80 ppm. The three different protons of the symmetrical aromatic ring of Schiff base ligand appear as a doublet at 7.02, as a doublet at 7.26 and as a singlet at 7.41 ppm. The singlet peak appearing at 8.40 ppm has been assigned to the azomethine (–HC=N–) proton.

An ORTEP view and the crystal packing of compound **I** are shown in Figs. 2 and 3, respectively. X-ray analysis shows that the compound is a mononuclear mercury(II) complex. In this complex, the four-coordinated Hg^{2+} ions are surrounded by two N atoms from ligand and two I atoms to form a distorted tetrahedral geometry.

The Hg–I distances 2.6867(2) and 2.6667(2) Å and Hg–N distances 2.355(2) and 2.396(2) Å are similar to the corresponding bond distances in related mononuclear mercury(II) complexes [16]. The C(2)=N(1) and C(12)=N(2) bond lengths of 1.278(3) and 1.280(3) Å conform to the values for a double bond while the bond lengths of C(1)–N(1) and C(11)–N(2) 1.469(4) and 1.475(4) Å conform to the value for a single bond. In complex **I**, the chelating bond angle N(1)Hg(1)N(2) is 74.83(7)°, i.e., almost the same as in related mononuclear mercury(II) complexes [16]. The four NHgI bond angles are found to be in the range 104°–120°, which are similar to those in mercury(II) complex $[Hg((Me\text{-}Cal)_2En)Br_2]$. However, the I(1)Hg(1)I(2) angle (124.991(7)°) has opened up due to the steric effect from the bulky I groups. The bond angles N(1)C(2)C(3), N(2)C(12)C(13), C(1)N(1)C(2), and C(11)N(2)C(12) are 125.2(3)°, 127.3(3)°, 118.4(2)°, and 116.5(2)°, respectively, and they are consistent with the sp^2 hybrid character for C(2), C(12), N(1), and N(2) atoms [16]. The Schiff base ligand $(3,4\text{-MeO-Bza})_2En$ adopts

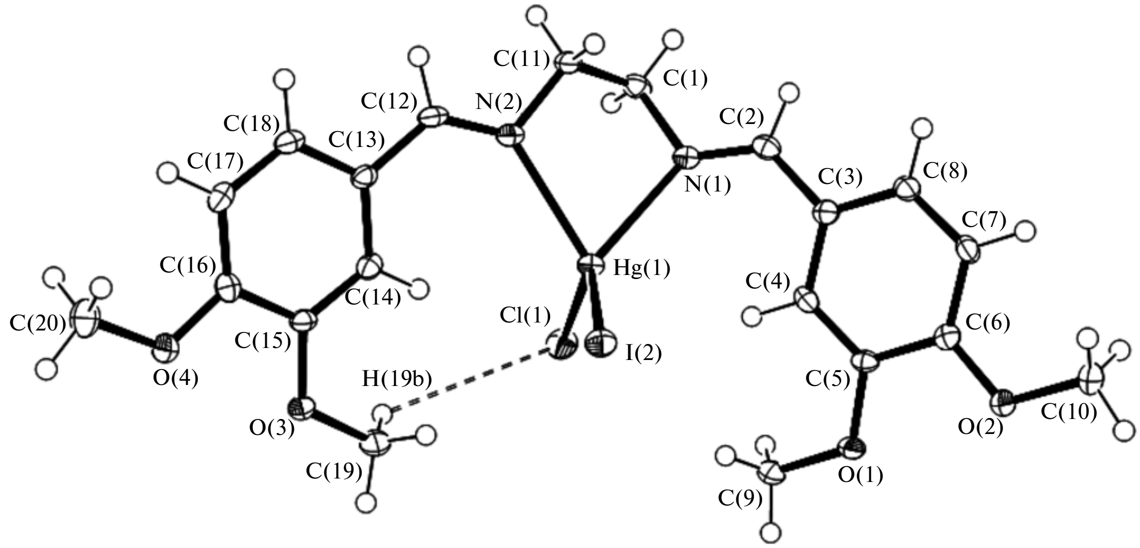

Fig. 2. Crystal structure of **I** with the atom numbering scheme.

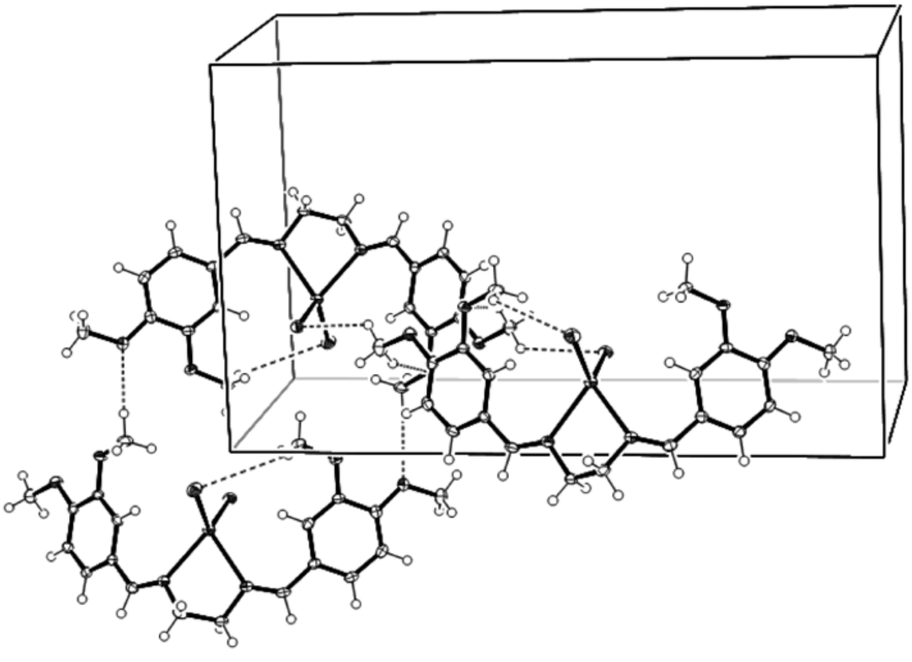

Fig. 3. Crystal packing of **I**.

an (*E*, *E*) configuration in this complex [18–20]. One non-classical intramolecular hydrogen bond of the type C(19)–H(19*b*)···I(1)–Hg is formed between methyl H atoms of ligand and halogen atom coordinated to metal ion (Fig. 2, Table 3). The $[Hg((3,4\text{-}MeO\text{-}Bza)_2En)I_2]$ molecules are eventually linked together via other non-classical intermolecular C–H···O and C–H···I hydrogen bonds (Fig. 3, Table 4). The dihedral angle between the planes defined by Hg–N–C–C–N and I–Hg–I is 79.471(65)°.

Table 3. Geometric parameters of hydrogen bonds of **I***

Contact D–H···A	Distance, Å			Angle D–H···A, deg
	D–H	H···A	D···A	
C(9)–H(9a)···O(4)^{i}	0.96	2.47	3.418(3)	170
C(19)–H(19b)···I(1)	0.96	3.433	4.091(4)	128
C(10)–H(10a)···I(2)	0.96	3.297	3.984	130
C(20)–H(20b)···O(1)	0.96	3.184	3.831	126

* Symmetry codes: $^{i}\,-x, -y + 1, -z + 1$.

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