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Diiodo{N,N'-Bis(2,3,4-Trimethoxybenzaldehyde)-Ethylenediimine}Mercury(II): Synthesis and Crystal Structure[1]

A. D. Khalaji[a, *], **K. Fejfarova**[b], **and M. Dusek**[b]

[a] *Department of Chemistry, Faculty of Science, Golestan University, Iran*

[b] *Institute of Physics of the ASCR, 18221 Prague 8, Czech Republic*

**e-mail: alidkhalaji@yahoo.com; ad.khalaji@gu.ac.ir*

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

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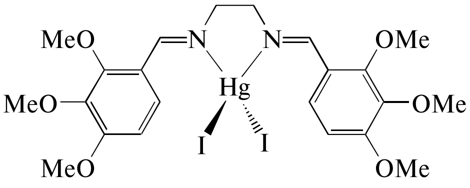
INTRODUCTION

The coordination chemistry of mercury(II) complexes with N and S donor ligands is of special interest in recent years, because of its 5d^{10} configuration may give rise to different coordination numbers and molecular and crystal structures [1–5]. Also mercury(II) complexes with polydentate ligands have been considerably investigated as potential luminescent materials [6]. Schiff base ligands have been used in constructing mercury(II) complexes of special structure [7–11]. In a continuation of our work on d^{10} complexes with bidenate Schiff base ligands [12–14], herein we obtained a new mononuclear mercury(II) complex, [Hg((2,3,4-MeO-Ba)$_2$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. X-ray powder diffraction pattern of the complex was recorded on a Bruker AXS diffractometer D8 ADVANCE with CuK_α radiation with nickel beta filter in the range 2θ = 10°–80°. Single-crystal X-ray diffraction was measured with Oxford diffraction four-circle diffractometer Gemini with MoK_α radiation.

Synthesis of (2,3,4-MeO-Ba)$_2$En. A solution of 2,3,4-trimethoxybenzaldehyde (3.92 g, 0.02 mol) in 25 mL of methanol was heated for 15 min at 50°C and then stirred for about 15 min. To this stirring solution, a solution of ethylenediamine (0.6 g, 0.01 mol) in 15 mL of methanol was added dropwise under constant stirring. The mixture was heated at about 50°C for 1.5 h and then allowed to cool for 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 of 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. The yield was 75%.

For $C_{22}H_{28}N_2O_6$			
anal. calcd., %:	C, 63.44;	H, 6.78;	N, 6.73.
Found, %:	C, 63.49;	H, 6.79;	N, 6.76.

Synthesis of I. To a stirring solution of the (2,3,4-MeO-Ba)$_2$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 and was then left at 273 K for several days without disturbance yielding suitable crystals of

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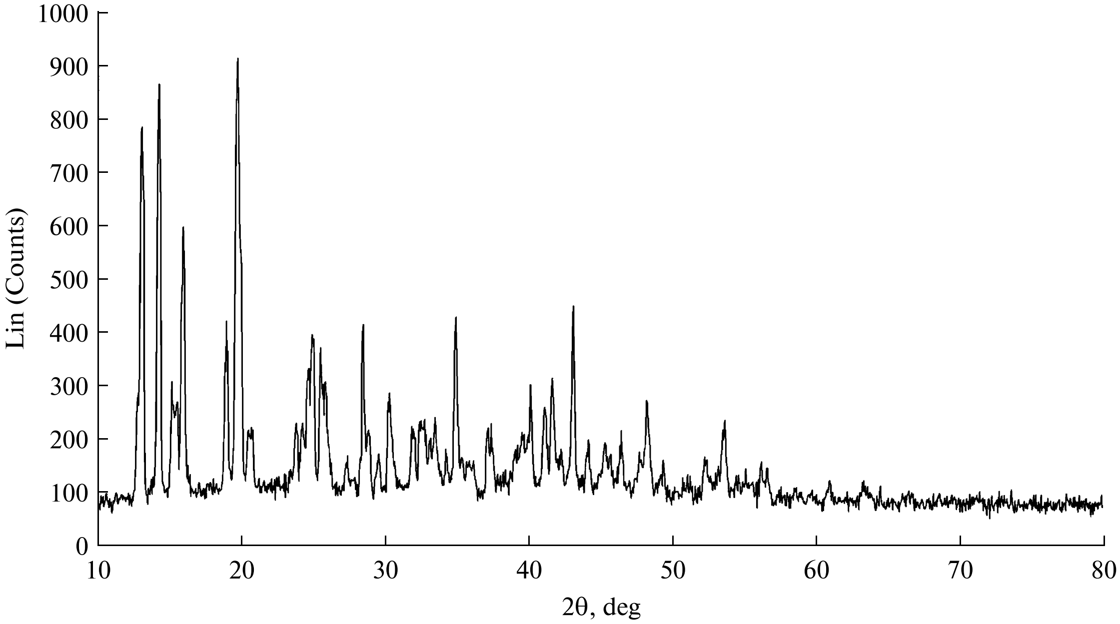

Fig. 1. Powder X-ray diffraction pattern of **I**.

I that subsequently were filtered off and washed with Et_2O. The yield was 62%.

For $C_{22}H_{28}N_2O_6I_2Hg$

anal. calcd., %:	C, 30.34;	H, 3.24;	N, 3.22.
Found, %:	C, 30.40;	H, 3.29;	N, 3.26.

X-ray structure determination. Preliminary identification of the sample was done with powder X-ray diffraction (Fig. 1). A single crystal of compound **I** with the dimensions 0.25 × 0.17 × 0.06 mm was chosen for X-ray diffraction study. Crystallographic measurements were done at 150 K with four-circle CCD diffractometer (Gemini of Oxford diffraction, Ltd.), using MoK_α radiation ($\lambda = 0.071073$ Å, graphite monochromator, area detector atlas). The crystal structures were solved by direct methods with the SIR2002 program [15] and refined with the Jana2006 program package [16] by the full-matrix least-squares technique on F^2. The molecular structure plots were prepared by ORTEP III [17]. 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. The isotropic atomic displacement parameters of hydrogen atoms were evaluated as $1.2U_{eq}$ of the parent atom. Crystallographic data and details of the data collection and structure refinements are summarized in Table 1. Selected bond distances and angles are listed in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 875048;

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

Parameter	Value
Formula weight	870.9
Crystal system	Monoclinic
Space group	*C*2/*c*
a, Å	10.7940(2)
b, Å	12.2032(2)
c, Å	20.1244(4)
β, deg	96.073(2)
V, $Å^3$	2635.94(8)
Z	4
F(000)	1632
ρ_{calcd}, g/cm^3	2.1938
Crystal size, mm	0.25 × 0.17 × 0.06
μ, mm^{-1}	8.23
θ Range, deg	2.8–26.38
Limiting indices *h*, *k*, *l*	$-13 \le h \le 13$, $-15 \le k \le 15$, $-25 \le l \le 25$
Reflection collected	18874
Independent reflections (R_{int})	2695 (0.034)
Reflections with $I > 3\sigma(I)$	2419
S	1.13
Number of parameters	154
$R (F^2 > 2\sigma(F^2))$	0.024
$wR (F^2)$	0.066
T_{min}/T_{max}	0.308/0.703
$\Delta\rho_{min}/\Delta\rho_{max}$, $e\,Å^{-3}$	−0.47/0.72

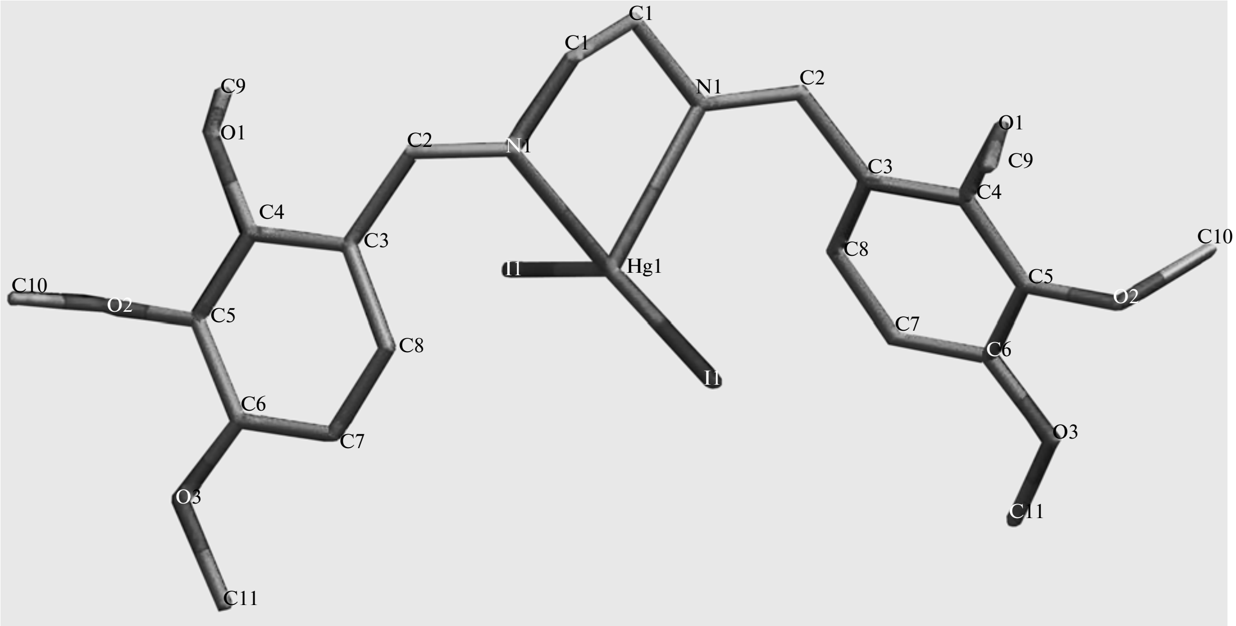

Fig. 2. Crystal structure of **I** with the atom numbering scheme.

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

Bond	d, Å	Bond	d, Å
Hg(1)–I(1)	2.6537(3)	Hg(1)–N(1)	2.402(3)
N(1)–C(1)	1.450(2)	N(1)–C(2)	2.279(5)
C(1)–C(1)^i	1.542(5)		
Angle	ω, deg	Angle	ω, deg
I(1)Hg(1)I(1)^i	146.50(2)	N(1)Hg(1)N(1)^i	72.47(10)
I(1)^{i}Hg(1)N(1)^i	103.26(8)	I(1)Hg(1)N(1)	103.26(8)
I(1)^{i}Hg(1)N(1)	103.62(7)	I(1)Hg(1)N(1)^i	103.62(7)
Hg(1)N(1)C(1)	111.3(2)	Hg(1)N(1)C(2)	125.1(3)
C(1)N(1)C(2)	121.9(3)		

deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

The bidenate Schiff base ligand (2,3,4-MeO-Ba)$_2$En was prepared under mild conditions. This ligand reacted with HgI$_2$ (molar ratio 1 : 1) in a mixture of methanol : chloroform (1 : 1 v/v) at 298 K to afford the corresponding mercury(II) complex **I** in 62% yield. An ORTEP view of compound **I** is shown in Fig. 2. X-ray analysis shows that it is a mononuclear mercury(II) complex. In this complex, the four-coordinated Hg^{2+} ions are surrounded by two N atoms from the Schiff base ligand and two **I** atoms to form a distorted tetrahedral geometry.

The Hg–I distance 2.6537(3) Å and Hg–N distance 2.402(3) Å are similar to the corresponding bond distances in related complexes [7–11]. In complex **I**, the chelating bond angle N(1)Hg(1)N(1)^i is 72.47(10)° and is almost the same as in related complexes [7–11]. The four NHgI bond angles are found to be in the range 103°, which are somewhat larger than those in a regular tetrahedron (109.5°). However, the I(1)Hg(1)I(1)^i angle (146.50(2)°) has opened up due to the steric effect from the bulky I groups.

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