

Synthesis and crystal structure of mercury (II) complex Hg (Meca₂en) I₂

A. Dehno Khalaji^{1*}, K. Fejfarova², M. Dusek²

1-Department of Chemistry, Faculty of Science, Golestan University, Iran

2-Institute of Physics of the ASCR, 182 21 Prague 8, Czech Republic

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Abstract: The mercury (II) complex, Hg (Meca₂en)I₂ (**1**), containing bidentate Schiff base ligand Meca₂en = *N,N'*-bis[(*E*)-2-benzylidenepropylidene]ethane-1,2-diamine, has been synthesized and characterized by elemental analyses (CHN) and ¹H-NMR spectroscopy. The crystal structure of **1** was determined using single-crystal X-ray diffraction. Structural investigation shows that **1** crystallizes in a monoclinic system, with space group *P*₂₁/*n*. The Schiff base ligand Meca₂en acts as a bidentate ligand coordinating *via* two N atoms to mercury (II) ion.

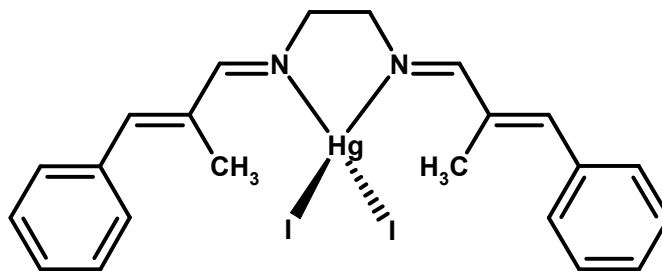
Keywords: Mercury (II) complex; Schiff base; Crystal structure; Monoclinic.

Introduction

During recent years, transition metal complexes of Schiff base ligands have received much attention [1-4]. These compounds play an important role in the development of coordination compounds, they have interesting properties and important applications in catalysis [5-8]. Many efforts have been devoted to the design and synthesis of new multidentate Schiff base ligands that are able to control the crystal structure and properties of transition metal complexes [9-11]. Most of the studies have been carried on four-coordinated

tetrahedral Zn(II) complexes of the type [M(L)X₂] where L is a bidentate Schiff base ligand [12-14], while Hg(II) complexes with these ligands are much less frequent [15,18].

In a continuation of our work on the preparation of transition metal complexes with bidentate Schiff-base ligands [12-14], here we report the synthesis and characterization of mercury(II) complex [Hg(Meca₂en)I₂] (**1**) with bidentate Schiff-base ligand *N,N'*-bis[(*E*)-2-benzylidenepropylidene] ethane-1,2-diamine (Scheme 1).



Scheme 1. Chemical structure of [Hg(Meca₂en)I₂] (**1**).

* Corresponding author, Tel: 0171-4427040, Fax: 0171-4427050, Email: ad.khalaji@gu.ac.ir

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. ^1H -NMR spectra were measured on a BRUKER DRX-500 AVANCE spectrometer at 500 MHz for the Schiff-base ligand and its complex. All chemical shifts are reported in δ units downfield from TMS.

Synthesis of $[\text{Hg}(\text{Meca}_2\text{en})\text{I}_2]$ (**1**)

The complex $[\text{Hg}(\text{Meca}_2\text{en})\text{I}_2]$ (**1**) was prepared by a simple reaction of the Meca_2en ligand and HgI_2 in methanol. To a stirring solution of the Meca_2en ligand [19] (0.2 mmol, in 5 mL chloroform) was added HgI_2 (0.2 mmol) in 10 mL methanol and the mixture was stirred for 10 min in air at room temperature and was then left at 298 K for several days without disturbance yielding suitable crystals of **1** that subsequently were filtered off and washed with Et_2O . Yield: 82%. Pale brown crystals. Anal. Calc. for $\text{C}_{22}\text{H}_{24}\text{N}_2\text{HgI}_2$: C, 34.28; H, 3.14; N, 3.63%. Found: C, 34.45; H, 3.21; N, 3.68%. ^1H -NMR (500 MHz, CDCl_3): δ 2.04 (s, 6H), 3.74 (s,

4H), 6.87 (s, 2H), 7.29 (t, 4H), 7.37-7.42 (m, 6H), 8.01 (s, 2H).

A single crystal of **1** was chosen for X-ray diffraction study. Crystallographic measurements were done at room temperature with four circle CCD diffractometer Gemini of Oxford diffraction, Ltd., using Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$), graphite monochromator and CCD detector Atlas. The crystal structure was solved by direct methods with program SIR2002 [20] and refined with program package Jana2006 [21] by full-matrix least-squares technique on F^2 . The molecular structure plots were prepared by ORTEP III [22]. 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 1.2Ueq of the parent atom. Crystallographic data and details of the data collection and structure refinements are listed in Table 1.

Table 1. Crystallographic data for **1**

Empirical formula	$\text{C}_{22}\text{H}_{24}\text{HgI}_2\text{N}_2$
Formula weight	770.8
Temperature	150
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 7.7182 (2) \text{ \AA}$
	$b = 12.1638 (3) \text{ \AA}$
	$c = 24.6286 (6) \text{ \AA}$
	$\beta = 91.045 (2)^\circ$
Volume	$2311.81 (10) \text{ \AA}^3$
μ	9.34 mm^{-1}
Z	4
Measured reflections	5680
Independent reflections	5677
Reflections with $I > 3\sigma(I)$	4280
Parameters	245
R_{int}	0.068
T_{min}	0.141
T_{max}	0.682
$R[F^2 > 3\sigma(F^2)]$	0.050
$wR(F^2)$	0.143
S	1.21
F_{000}	1424
$\Delta\rho_{\text{max}}$	1.81 e \AA^{-3}
$\Delta\rho_{\text{min}}$	-1.61 e \AA^{-3}

Results and discussion

^1H -NMR

The ^1H -NMR spectrum was recorded using DMSO- d_6 as solvent at 500 MHz. The aromatic (HAr-C) and olefinic (ph-CH=C-) protons appeared at 7.27-7.42 and 6.87 ppm, respectively, and the aliphatic protons (-CH₃ and -CH₂-CH₂-groups) appeared at 2.04 and 3.74 ppm as single signal, respectively. The protons of azomethine groups (-CH=N-) appeared at 8.01 ppm as single signal.

Crystal structure description

Crystals of **1** suitable for X-ray crystallography were obtained by slow evaporation of solvent at 298 K after about one week. The molecular structure including the atom-numbering scheme and view of packing diagram of **1** are shown in Figs 1 and 2, respectively. Selected bond lengths and angles are listed in Table 2. Complex **1** crystallizes in monoclinic system with space group of $P2_1/n$. The mercury(II) ion in **1** is tetrahedrally

coordinated by two azomethine nitrogen atoms of Schiff base and two iodide atoms. The coordination about mercury (II) ion is considerably distorted due to the restricting bite angle of the chelating Schiff base ligand. The N(1)-Hg(1)-N(2) angle is only $75.981(1)^\circ$ in **1**, being below the usual range of 82 - 90° found for other ethylenediamine-chelated transition metal complexes [12-18]. On the contrary, the I(1)-Hg(1)-I(2) bond angle ($129.34(3)^\circ$) is much larger than those of tetrahedral complexes due to the steric effects from the bulky iodo groups. The average of Hg-N (2.43 Å) and Hg-I (2.67 Å) bond lengths in **1** agrees well with corresponding values in other mercury(II) complexes [15-18]. Possible weak inter- and intramolecular C-H...I hydrogen bonds formed between aromatic and aliphatic hydrogen atoms of the bidentate Schiff base ligand and the coordinated iodide atoms are indicated in Figs. 1 and 2 and listed in Table 3.

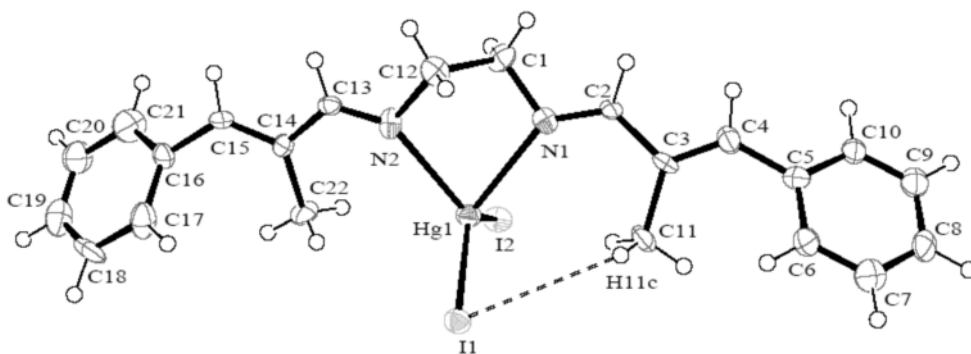


Fig. 1. An ORTEP view of **1**. Ellipsoids are drawn from 50% probability label. Hydrogen bonds are shown as dashed lines.

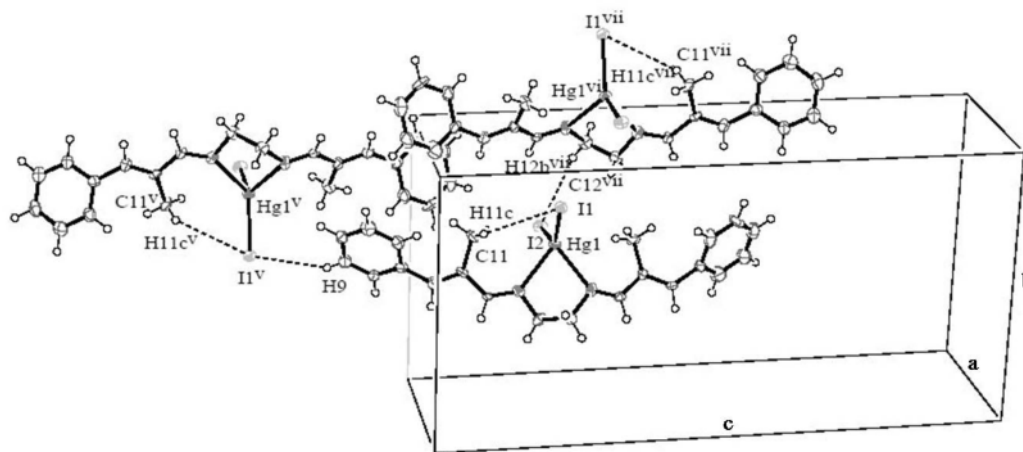


Fig. 2. Unit cell packing diagram of **1**. Hydrogen bonds are shown as dashed lines.

Table 2 Selected bond geometric parameters (Å, °).

Hg1—I1	2.6640(9)	Hg1—I2	2.6824(8)
Hg1—N1	2.441(9)	Hg1—N2	2.417(8)
N1—C1	1.474(17)	N1—C2	1.296(16)
N2—C12	1.517(16)	N2—C13	1.270(16)
C2—C3	1.470(16)	C13—C14	1.425(16)
C3—C4	1.300(18)	C14—C15	1.337(18)
C4—C5	1.490(18)	C15—C16	1.510(18)
I1—Hg1—I2	129.34(3)	N1—Hg1—N2	75.981(1)
I1—Hg1—N1	116.93(4)	I2—Hg1—N1	97.60(4)
I1—Hg1—N2	109.90(4)	I2—Hg1—N2	113.87(4)
C12—N2—C13	117.6(10)	C1—N1—C2	115.2(10)
N1—C1—C12	109.4(10)	N1—C2—C3	126.1(11)
N2—C12—C1	111.7(8)	N2—C13—C14	125.9(10)

Table 3 Intra- and inter-molecular hydrogen bonds geometry for 1.

D-H...A	D-H	H...A	D...A	D-H...A
C(1)-H(12b)...I(2)	0.960	3.219	4.116	156.389
C(11)-H(11c)...I(1)	0.960	3.394	4.114	133.469
C(9)-H(9)...I(1)	0.959	3.250	4.006	137.065

The ligand Meca₂en adopts an (E,E) configuration in this complex [14]. Despite the fact that the donor azomethine nitrogen atoms are sp²-hybridized, the chelate ring is significantly puckered in 1, and some strain in the chelate ring is suggested by deviation from 120° angle about the nitrogen atoms (see Table 2). The angles between the plane of the Ph rings, C(5)-C(10) and C(16)-C(21), and the plane subtended by C(5)-C(4)-C(3)-C(2) or C(16)-C(15)-C(14)-C(13) are 40.86° and 52.44°, respectively.

Supplementary data

Crystallographic data (excluding structure factors) for the structure reported in this paper has been deposited with the Cambridge Crystallographic Center, CCDC No. 860845. 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 336 033, e-mail:

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

or

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