

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

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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.

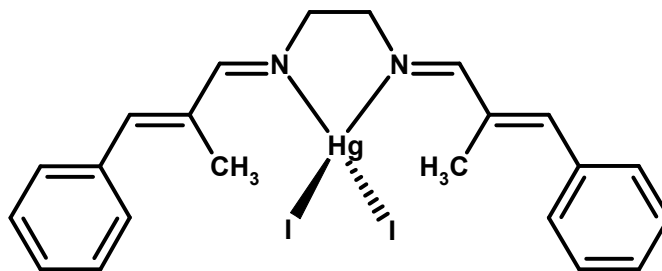
Keywords: Mercury (II) complex; Schiff base; Crystal structure; Monoclinic.

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**).

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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. $^1\text{H-NMR}$ 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%. $^1\text{H-NMR}$ (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 $\text{Mo K}\alpha$ 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-d₆ 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 P2₁/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)° 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)°) 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.

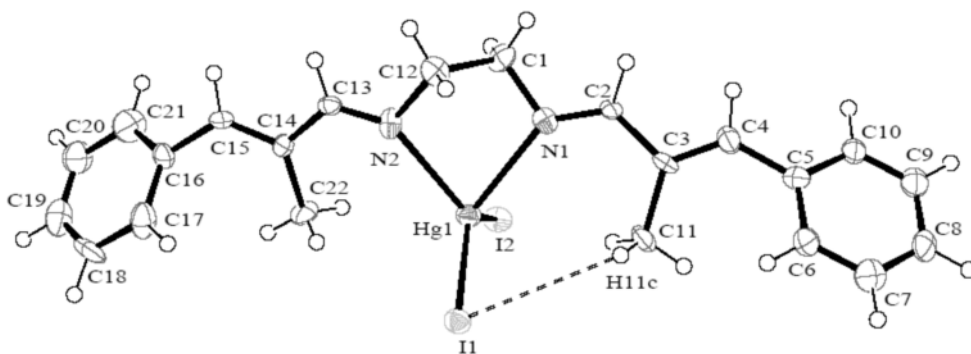


Fig. 1. An ORTEP view of **1**. Ellipsoids are drawn from 50% probability label. Hydrogen bonds are shown as dashed lines.

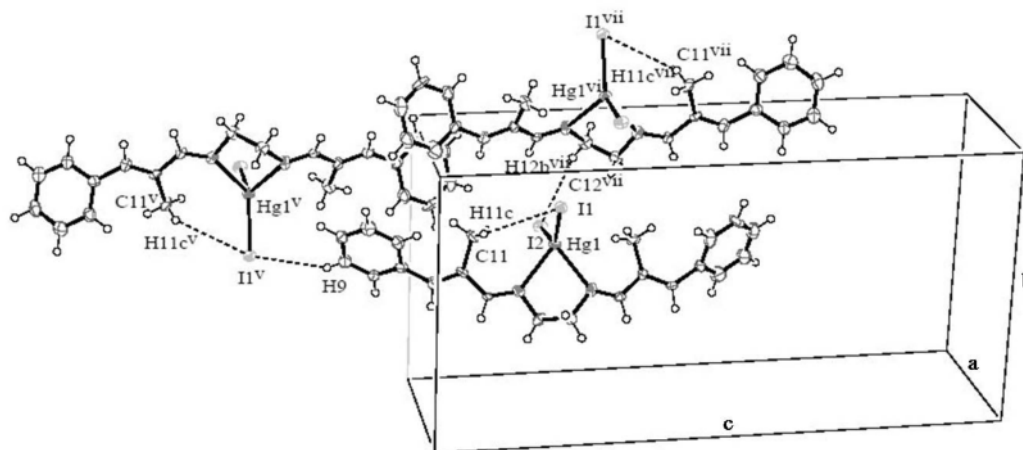


Fig. 2. Unit cell packing diagram of **1**. Hydrogen bonds are shown as dashed lines.

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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References

- [1] Laye R.H., "Syntheses and photophysical properties of a series of [2:2] silver(I) metallocycles", *Inorganica Chimica Acta* 360 (2007) 439-447.
- [2] Zhang G., Yang G., Ma J.S., "A novel luminescent metallomacrocyclic assembled by silver nitrate and 1,3-bis(pyrrol-2-yl-methyleneamino)propane", *Inorganic Chemistry Communications* 7 (2004) 994-997.

- [3] Dolaz M., McKee V., Golcu A., Tumer M., "Synthesis, structural characterization, thermal and electrochemical studies of the *N,N'*-bis[(3,4-dichlorophenyl)methylidene]cyclohexane-1,4-diamine and its Cu(II), Co(II) and Ni(II) metal complexes", *Spectrochimica Acta A* 71 (2009) 1648-1654.
- [4] Mukherjee A., Chakrabarty R., Ng S.W., Patra G.K., "The syntheses, characterizations, X-ray crystal structures and properties of Cu(I) complexes of a bis-bidentate schiff base ligand", *Inorganica Chimica Acta* 363 (2010) 1707-1712.
- [5] Ardizzoia G.A., Brenna S., Castelli F., Galli S., "Copper(I)-imine complexes: Synthesis and catalytic activity in olefin cyclopropanation", *Inorganica Chimica Acta* 362 (2009) 3507-3512.
- [6] Sawant S.K., Gaikwad G.A., Sawant V.A., Yamgar B.A., Chavan S.S., "Synthesis, characterization and catalytic study of Schiff base copper(I) complexes for the amination of aryl halide", *Inorganic Chemistry Communications* 12 (2009) 632-635.
- [7] Chattopadhyay S., Bhar K., Khan S., Mitra P., Butcher R.J., Ghosh B.K., "Synthesis, structure and luminescence behaviour of bis(tridentate) Schiff base bridged dinuclear lead(II) pseudohalides", *Journal of Molecular Structure* 966 (2010) 102-106.
- [8] Shi Q., Xu L., Ji J., Li Y., Wang R., Zhou Z., Cao R., Hong M., Chan A.S.C., "Syntheses and structures of two anion-templated dinuclear cadmium complexes with diamino-binaphthyl Schiff bases as ligands", *Inorganic Chemistry Communications* 7 (2004) 1254-1257.
- [9] Chowdhury H., Ghosh R., Rahaman S.H., Ghosh B.K., "Syntheses, X-ray structures and properties of a dinuclear cadmium(II) azido and a polymeric cadmium(II) thiocyanato compounds containing bis(tridentate) congregators", *Polyhedron* 26 (2007) 5023-5029.
- [10] Morshedi M., Amirnasr M., Slawin A.M.Z., Woollins J.D., Khalaji A.D., "Synthesis and coordination chemistry of new tetradentate N₂S₂ donor Schiff-base ligand *ca*²-dapte: Mononuclear and dinuclear copper (I) complexes [Cu(*ca*²dapte)] ClO₄ and [Cu(*ca*²dapte)]₂(X)₂(*ca*²dapte) (X = I and Br)", *Polyhedron* 28 (2009) 167-171.
- [11] Komatsu H., Ochiai B., Hino T., Endo T., "Thermally latent reaction of hemiacetal ester with epoxide controlled by Schiff-base-zinc chloride complexes with tunable catalytic activity", *Journal of Molecular Catalysis A Chemical* 273 (2007) 289-297.
- [12] Khalaji A.D., Grivani G., Rezaei M., Fejfarova K., Dusek M., "Synthesis and spectral characterization of mercury(II) complexes with the bidentate Schiff base ligand *N,N'*-bis(2,3-dimethoxybenzylidene)-1,2-diaminoethane: The crystal structures of [Hg((23-MeO-ba)2en)I₂] and [Hg((23-MeO-ba)2en)Br₂]", *Polyhedron* 30 (2011) 2790-2794.
- [13] Amirnasr M., Mahmoudkhani A.H., Gorji A., Dehghanpour S., Bijanzadeh H.R., "Cobalt(II), nickel(II), and zinc(II) complexes with bidentate *N,N'*-bis(β-phenylcinnamaldehyde)-1,2-diiminoethane Schiff base: synthesis and structures", *Polyhedron* 21 (2002) 2733-2742.
- [14] Khalaji A.D., Weil M., Grivani G., Jalali Akerdi S., "Synthesis, characterization, and crystal structure of two zinc (II) halide complexes with the symmetrical bidentate Schiff-base ligand (3,4-MeO-ba)2en", *Monatshefte Chemistry* 141 (2010) 539-543.
- [15] Montazerzohori M., Khani S., Tavakol H., Hojjati A., Kazemi M., "Synthesis, spectroscopic and thermal studies of some IIB group complexes with a new N₂-Schiff base ligand", *Spectrochimica Acta A* 81 (2011) 122-127.
- [16] Montazerzohori M., Joohari S., Musavi S.A., "Synthesis and spectroscopic studies of some cadmium (II) and mercury (II) complexes of an asymmetrical bidentate Schiff base ligand", *Spectrochimica Acta A* 73 (2009) 231-237.
- [17] Drew M.G.B., De S., Datta D., "Stereochemically non-rigid helical mercury (II) complexes", *Inorganica Chimica Acta* 362 (2009) 2487-2491.
- [18] Chattopadhyay S., Bhar K., Das S., Satapathi S., Fun H.K., Mitra P., Ghosh B.K., "Synthesis, molecular and crystalline architectures, and properties of novel bis(bidentate) and

bis(tridentate) Schiff base bridged dinuclear mercury(II)pseudohalides: Control of coordination numbers by varying denticities", Polyhedron 29 (2010) 1667-1675.

[19] Khalaji A.D., Ng S.W., "*N,N'*-Bis[(*E*)-2-Benzylidenepropylidene]-ethane-1,2-diamine" Acta Crystallographica E64 (2008) o1771.

[20] Burla M.C., Camalli M, Carrozzini B, Cascarano G, Giacovazzo C, Polidori G, Spagna R., "*SIR2002 : the program*", Journal of Applied Crystallography 36 (2003) 1103.

[21] Petricek V, Dusek M, Palatinus L. Jana2006., "*Structure determination software programs*". Institute of Physics, Praha, Czech Republic (2008).

[22] Farrugia L.J., "*ORTEP-3 for Windows - a version of ORTEP-III with a Graphical User Interface (GUI)*", Journal of Applied Crystallography 30 (1997) 565.