Synthesis and Crystal Structure of Bis[1,3-bis(2-methoxyphenyl)triazene]mercury(II)

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The crystal structure of [HgL₂], L = 1,3-bis(2-methoxyphenyl)triazene was determined by X-ray diffraction. The complex crystallizes in the orthorhombic system, space group *Pna*2₁ with *a* = 8.1817(3), *b* = 15.4123(6), *c* = 21.1836(8) Å, *V* = 2671.23(17) Å³, *Z* = 4. The structure was solved by the full-matrix least-squares on *F*², and had a refined *R* value of 0.0274 for 6187 reflections (*I* > 2σ(*I*)). The Hg atom is coordinated by two molecules of the title ligand *via* the N(3), N(4) and N(6) atoms in a distorted triangular pyramid geometry.

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Triazenes are a class of compounds characterized by the presence of a diazoamino functional group (N=N-N). The simplest member of this family is known as just triazene. The coordination properties of the triazene ligand with Aryl groups as 1,3-substituents (Ar-N=N-NH-Ar) have been intensely studied during the past years. Coordination was found to be *N*₁-monodentate, *N*₁,*N*₃-chelating and *N*₁,*N*₃-bridging ligand. These compounds have been used in a variety of ways, ranging from transition metal complexes and polymer synthesis to anticancer drugs.

The compound 1,3-bis(2-methoxyphenyl)triazene as one of the triazene family can act as a ligand in transition-metal complexes which prepared and its crystal structure reported.¹ Recently, a complex containing the title ligand and Hg(II) cation was synthesized and its crystal structure reported.² In this complex one Cl atom on HgCl₂ salt was replaced by L and a tetrahedral geometry was formed. In addition, a complex containing four molecules of L and four Ag(I) atoms was synthesized and its crystal structure and solution studies reported.³

In this paper, we report on the synthesis of the [HgL₂] complex

of the title ligand and discussed the basis of experimental results, especially the X-ray diffraction data concerning the crystal and molecular structure of the compound (Fig. 1).

The title complex was synthesized as follows: under stirring conditions, triethylamine (0.7 mmol, 0.25 ml) was added to a dichloromethane solution of ligand (1 mmol, 0.25 g) and then a suspension solution of mercury(I) nitrate (0.5 mmol, 0.15 g) in methanol was added dropwise. After mixing for 15 min at room temperature the solution was heated to 40°C for 10 min and filtered. After 24 h red and air-stable needle-like crystals were formed. M. P. = 126 – 128°C

The crystal structure of the title compound was determined by direct methods and refined on *F*² by full-matrix least-squares using the program SHELXTL-98.⁴ An X-ray diffraction study of the compound showed that it crystallized in the orthorhombic system with the *Pna*2₁ space group.

Crystal data and details of the data collection are summarized in Table 1. The atomic coordinates of nonhydrogen atoms are given in Table 2, and selected atomic distances and bond angles are summarized in Table 3.

The molecular structure of the title complex and the atomic numbering scheme are shown in Fig. 2. Concerning the molecular structure of the complex, Hg cation is coordinated by

Fig. 1 Chemical structure of HgL₂.

Fig. 2 ORTEP drawing of the molecule structure HgL₂ (50% probability level).

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Table 1 Crystal data and structure refinement details for [HgL₂]

Formula: C ₂₈ H ₂₈ HgN ₆ O ₄
Formula weight = 713.15
Crystal system: orthorhombic
Space group: <i>Pna</i> 2 ₁ <i>Z</i> = 4
<i>T</i> = 100 K
<i>a</i> = 8.1817(3) Å
<i>b</i> = 15.4123(6) Å
<i>c</i> = 21.1836(8) Å
<i>V</i> = 2671.23(17) Å ³
<i>D</i> _x = 1.773 g/cm ³
No. of reflections used = 6187
2 θ _{max} = 58.00 with Mo <i>K</i> α
<i>R</i> = 0.0274, <i>wR</i> 2 = 0.0634
(Δ / σ) _{max} = 0.009
($\Delta\rho$) _{max} = 1.289
($\Delta\rho$) _{min} = -0.632 e. Å ⁻³
Measurement: Bruker APEX2 CCD area detector
Program system: APEX II, version 2.0-1; SAINT, version 7.23A;
SADABS, version 2004/1; XPREP, version 2005/2;
SHELXTL, version 6.1.
Structure determination: SHELXS97
Refinement: full-matrix least-squares on <i>F</i> ²

CCDC 665839 contains the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk

Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for [HgL₂], *L* = 1, 3-bis(2-methoxybenzene)triazene. *U*(eq) is defined as one third of the trace of the orthogonalized *U*_{ij} tensor.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
Hg(1)	8111(1)	5425(1)	2500(1)	23(1)
N(1)	9482(4)	5935(2)	1317(2)	24(1)
N(2)	8822(4)	5227(2)	1146(2)	25(1)
N(3)	8114(4)	4822(2)	1625(2)	22(1)
N(4)	5555(4)	5262(2)	3259(2)	27(1)
N(5)	6456(5)	5617(2)	3671(2)	28(1)
N(6)	7875(4)	5864(2)	3424(2)	24(1)
O(1)	9833(4)	7652(2)	1321(2)	30(1)
O(2)	7428(3)	3642(2)	2511(3)	30(1)
O(3)	3499(4)	4758(2)	2394(2)	30(1)
O(4)	10522(4)	6558(2)	2906(1)	29(1)
C(1)	10453(5)	6326(3)	835(2)	26(1)
C(2)	10644(5)	7230(3)	847(2)	26(1)
C(3)	11592(5)	7633(3)	390(2)	30(1)
C(4)	12389(6)	7139(3)	-73(2)	32(1)
C(5)	12228(5)	6245(3)	-75(2)	32(1)
C(6)	11268(6)	5839(3)	375(2)	29(1)
C(7)	10111(6)	8561(3)	1371(3)	39(1)
C(8)	7002(5)	4151(3)	1476(2)	27(1)
C(9)	6603(6)	3546(3)	1945(2)	28(1)
C(10)	5447(6)	2898(3)	1831(2)	32(1)
C(11)	4732(6)	2846(3)	1235(3)	39(1)
C(12)	5147(6)	3422(3)	765(2)	38(1)
C(13)	6263(6)	4083(3)	885(2)	31(1)
C(14)	6844(6)	3146(4)	3043(3)	39(1)
C(15)	4040(5)	4943(3)	3472(2)	25(1)
C(16)	2960(6)	4654(3)	3005(3)	27(1)
C(17)	1452(6)	4293(3)	3163(2)	29(1)
C(18)	1043(6)	4229(3)	3800(2)	32(1)
C(19)	2093(6)	4508(3)	4270(3)	34(1)
C(20)	3592(6)	4863(3)	4104(2)	31(1)
C(21)	2410(8)	4527(3)	1896(3)	34(1)
C(22)	9080(5)	6194(3)	3831(2)	24(1)
C(23)	10485(5)	6560(2)	3549(2)	25(1)
C(24)	11712(5)	6894(3)	3937(2)	32(1)
C(25)	11540(6)	6859(3)	4587(2)	34(1)
C(26)	10171(6)	6491(3)	4861(2)	34(1)
C(27)	8945(5)	6164(3)	4482(2)	30(1)
C(28)	11928(5)	6924(3)	2603(3)	34(1)

Table 3 Selected bond length (Å) and bond angles (°) distance.

Atoms	Distances
Hg(1)–N(3)	2.073(4)
Hg(1)–N(4)	2.650(4)
Hg(1)–N(6)	2.081(4)
N(1)–N(2)	1.270(5)
N(2)–N(3)	1.323(5)
N(4)–N(5)	1.268(5)
Angles	
N(5)–N(6)–Hg(1)	111.0(3)
N(2)–N(3)–Hg(1)	118.3(3)
N(5)–N(4)–Hg(1)	85.3(2)
N(4)–N(5)–N(6)	111.1(4)
N(3)–Hg(1)–N(6)	170.83(14)
N(3)–Hg(1)–N(4)	120.09(12)
N(6)–Hg(1)–N(4)	52.16(12)

Fig. 3 Crystal packing fragment along the *a* crystal axes. Hydrogen atoms are not depicted for clarity (●; centroid).

two molecules of the title ligand. The bond angles are N(6)–Hg(1)–N(4) = 52.16(12)°, N(3)–Hg(1)–N(6) = 170.83(14)°, N(3)–Hg(1)–N(4) = 120.09(12)°. Thus, this asymmetric complex is coordinated in the distorted triangular pyramid geometry.

According to the best structure of the diazoamino group (N=N–N), the two nitrogen atoms of each ligand can be coordinated to the Hg ion,⁵ but in this complex because of a long distance between the Hg ion and N(1) (Hg(1)···N(1) = 2.856(4) Å), this atom could not coordinate to the metal, whereas the other mercury nitrogen bond distances (Hg(1)–N(3) = 2.073(4), Hg(1)–N(4) = 2.650(4) and Hg(1)–N(6) = 2.081(4) Å) in HgL₂ are well below the upper limit of the typical Hg–N covalent band (2.75(2) Å).⁶ Also, due to the distortion of one of the coordinated ligands during complexation, long distances between the oxygen atoms and mercury ion (*e.g.* Hg(1)···O(2) = 2.803(5) and Hg(1)···O(1) = 2.772(5) Å), as well as the angle strain, none of the oxygen atoms of the ligand could be coordinated to the Hg cation. An important feature of the title complex is the presence of π – π stacking interactions. As shown in Fig. 3, the π – π stacking between aromatic rings Cg1[Cg1: C15–C20] and Cg2[Cg2: C22–C27] (*x*–1, *y*, *z*) with distances of 3.704 Å is observed.

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