Crystal Structure of a Novel Complex of 1,3-Bis(2-methoxybenzene)triazene with Mercury(II)

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The crystal structure of $[\text{ClHgL}]$, $\text{L} = 1,3\text{-bis}(2\text{-methoxybenzene})\text{triazene}$ was determined by X-ray diffraction. The complex crystallizes in the triclinic system, space group $P\bar{1}$ with $a = 9.2614(5)$, $b = 11.4127(6)$, $c = 16.3378(9)\text{\AA}$, $\alpha = 110.401(5)^\circ$, $\beta = 106.075(5)^\circ$, $\gamma = 90.302(5)^\circ$, $V = 1545.3(2)\text{\AA}^3$, $Z = 4$. The structure was solved by the direct method (SHELXTL-98) and had refined R value of 0.0361 for 4709 reflections ($I > 2\sigma(I)$). The Hg atom is coordinated by a Cl atom as well as O, N and N atoms of the ligand in a tetrahedral geometry.

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Recently, the 1,3-bis(2-methoxybenzene)triazene ligand was synthesized and its crystal structure reported.¹ Structural and solution studies of a novel tetranuclear silver(I) cluster of this ligand ($[\text{AgL}]_4 \cdot \text{THF}$) have also been reported.² In this paper, we report on the synthesis of the $[\text{ClHgL}]$ complex of this ligand and discuss the basis of the 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: a methanol solution of ligand (0.2573 g, 0.001 mol) was added to a solution of mercury(II) chloride

(0.2715 g, 0.001 mol). After mixing for one hour at room temperature, an orange precipitate was formed, filtered and washed with methanol (3 times, each time with 2 ml), and then

Table 1 Crystal data and structure refinement details for $[\text{ClHgL}]$, $\text{L} = 1,3\text{-bis}(2\text{-methoxybenzene})\text{triazene}$

Formula: $\text{C}_{14}\text{H}_{14}\text{ClHgN}_3\text{O}_2$
Formula weight = 492.32
Crystal system: triclinic
Space group: $P\bar{1}$ $Z = 4$
$a = 9.2614(5)\text{\AA}$
$b = 11.4127(6)\text{\AA}$
$c = 16.3378(9)\text{\AA}$
$\alpha = 110.401(5)^\circ$
$\beta = 106.075(5)^\circ$
$\gamma = 90.302(5)^\circ$
$V = 1545.3(2)\text{\AA}^3$
$D_x = 2.116 \text{ g/cm}^3$
$F(000) = 928$
Absorption coefficient ($\text{Mo } K\alpha$) = 10.140 mm^{-1}
$T = 100 \text{ K}$
Crystal size (mm) = $0.39 \times 0.23 \times 0.18$
$\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$
$R = 0.0361$
$R_w = 0.0833$
$(\Delta/\sigma)_{\text{max}} = 0.000$
$(\Delta\rho)_{\text{max}} = 2.397 \text{ e\AA}^{-3}$
$(\Delta\rho)_{\text{min}} = -1.048 \text{ e\AA}^{-3}$
θ range for data collection: 1.91 to 29.00°
Completeness to $\theta = 29.00$ 98.7%
Max. and min. transmission: 0.164 and 0.0812
Goodness-of-fit on $F^2 = 1.057$
No. of reflections used = 16825
No. of parameters = 407
Refinement method: full-matrix least-square on F^2
Absorption correction: semi-empirical from equivalents
Program system: SHELXTL-98 ³
Data collection: APEX2; Bruker, 2005
Cell refinement and data reduction: APEX2; Bruker, 2005
CCDC = 624144 contains the supplementary crystallographic data for this paper.

Fig. 1 Chemical structure of the title compound.

Fig. 2 ORTEP drawing of the molecule structure $[\text{ClHgL}]$ (thermal ellipsoids drawn at 50% probability).

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

Atoms	x	y	z	$U(\text{eq})$
Hg(1)	7773(1)	7071(1)	9962(1)	36(1)
Cl(1)	5523(2)	7468(2)	10269(1)	56(1)
O(1)	7617(4)	4637(3)	8859(2)	37(1)
O(2)	9543(4)	10677(3)	11462(2)	40(1)
N(1)	9738(5)	6605(4)	9609(3)	33(1)
N(2)	10797(5)	7583(4)	9959(3)	32(1)
C(1)	8966(6)	4407(4)	8678(3)	33(1)
C(2)	10096(6)	5458(4)	9075(3)	32(1)
N(3)	10330(5)	8569(4)	10435(3)	34(1)
C(3)	11497(6)	5296(5)	8922(3)	36(1)
C(4)	11784(6)	4120(5)	8391(4)	41(1)
C(5)	10665(7)	3097(5)	7996(4)	42(1)
C(6)	9257(6)	3249(5)	8137(3)	37(1)
C(7)	6534(6)	3581(5)	8605(4)	41(1)
C(8)	10954(6)	10767(5)	11373(3)	35(1)
C(9)	11402(6)	9655(4)	10823(3)	33(1)
C(10)	12813(6)	9678(5)	10690(3)	38(1)
C(11)	13816(6)	10780(5)	11105(3)	39(1)
C(12)	13388(7)	11866(5)	11664(3)	41(1)
C(13)	11975(7)	11865(5)	11793(3)	39(1)
C(14)	9026(7)	11801(5)	11973(4)	45(1)
C(1A)	6082(5)	5568(4)	6320(3)	31(1)
Hg(1A)	7405(1)	7161(1)	5201(1)	33(1)
Cl(1A)	9767(2)	7311(2)	5044(2)	49(1)
O(1A)	7455(4)	5664(3)	6164(2)	36(1)
O(2A)	5629(4)	8939(4)	3512(2)	40(1)
N(1A)	5394(5)	6973(4)	5501(3)	33(1)
N(2A)	4338(5)	7555(4)	5114(3)	33(1)
C(2A)	4993(5)	6275(4)	5975(3)	32(1)
C(3A)	3572(6)	6231(5)	6110(3)	37(1)
N(3A)	4844(5)	8084(4)	4660(3)	32(1)
C(4A)	3248(6)	5499(5)	6574(4)	41(1)
C(5A)	4316(6)	4806(5)	6906(3)	40(1)
C(6A)	5745(6)	4850(5)	6785(3)	36(1)
C(7A)	8546(6)	4873(5)	6425(4)	38(1)
C(8A)	4237(6)	9196(4)	3621(3)	35(1)
C(9A)	3792(6)	8741(4)	4228(3)	32(1)
C(10A)	2396(6)	8988(4)	4377(3)	35(1)
C(11A)	1439(6)	9629(5)	3930(3)	38(1)
C(12A)	1856(6)	10044(4)	3315(3)	38(1)
C(13A)	3245(6)	9837(5)	3163(3)	38(1)
C(14A)	6187(7)	9523(6)	2995(4)	48(1)
Hg(1'')	7081(4)	7697(3)	4768(3)	73(1)
Cl(1'')	9480(30)	7380(20)	4668(5)	61(6)
Hg(1')	8114(10)	7983(9)	10351(8)	64(2)

Table 3 Selected bond length [$\text{\AA}$] and bond angles [$^\circ$]

Hg(1)-N(1)	2.075(4)
Hg(1)-Cl(1)	2.2865(14)
Hg(1)-N(3)	2.674(4)
Hg(1)-O(1)	2.710(4)
N(1)-N(2)	1.329(6)
N(2)-N(3)	1.280(6)
N(1)-Hg(1)-Cl(1)	176.16(12)
N(1)-Hg(1)-N(3)	51.92(14)
Cl(1)-Hg(1)-N(3)	131.66(10)
N(1)-Hg(1)-O(1)	66.16(13)
Cl(1)-Hg(1)-O(1)	110.21(9)
N(3)-Hg(1)-O(1)	118.07(12)
N(2)-N(1)-Hg(1)	112.4(3)
N(3)-N(2)-N(1)	110.8(4)

atoms (Hg(1')-N(3) and Hg(1'')-N(3A)). Each disordered Hg atom participate in additional contacts with only one of the methoxy groups, which are almost equivalent in the ligand (Hg(1)-O(1), Hg(1')-O(2), Hg(1A)-O(1A), Hg(1'')-O(2A)). Also, the chlorine atoms are disordered (Cl(1A) and Cl(1'')). Although it might be suggested that the Cl(1) atom is also disordered, it was impossible to resolve that disorder. Thus, the geometry of the molecule is a distorted tetrahedral with the C1 symmetry group. The facts were verified by an X-ray diffraction study of a single crystal of the title compound (Fig. 2).

The Hg(1)-Cl(1) bond distance in the complex is 2.2865(14) $\text{\AA}$, which is close to the same distance in HgCl_2 (2.25 $\text{\AA}$).⁶ The Hg(1)-N(1) bond distance is 2.075(4) $\text{\AA}$. This value is comparable to the corresponding bond distance value of ClHgR ($\text{R} = 2,6\text{-pyridinediamine}$).⁷

Crystal and experimental data are listed in Table 1. The final atomic coordinates for the non-hydrogen atoms are given in Table 2, and selected bond lengths and angles are summarized in Table 3.

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References

1. M. K. Rofouei, M. Shamsipur, M. Payehghadr, *Anal. Sci.*, **2006**, 22, x79.
2. M. Payehghadr, M. K. Rofouei, A. Morsali, M. Shamsipur, *Inorg. Chim. Acta*, **2007**, 360, 1792.
3. G. M. Sheldrick (1998). SHELXTL v. 5.10. Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA.
4. D. D. Moore and S. D. Robinson, *Adv. Inorg. Chem. Radiochem.*, **1986**, 30, 1.
5. M. B. Hursthouse, M. A. Mazid, T. Clark, and S. D. Robinson, *Polyhedron*, **1993**, 12, 563.
6. F. A. Cotton, G. Wilkinson, C. A. Murillo, and M. Bochmann, "Advanced Inorganic Chemistry", 8th ed., **1999**, John Wiley and Sons, New York.
7. M. Ranjbar and H. Aghabozorg, *Anal. Sci.*, **2004**, 20, x154.

dried in air. The orange crude material (0.3654 g) was dissolved in 10 ml of THF, and placed in a freezer. After two weeks beautiful red and air-stable needle-like, single crystal of title complex was formed; yield, 0.2 g, 41%, M.P. 152 - 154 $^\circ\text{C}$.

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-98.³

An X-ray diffraction study of the compound showed that it crystallized in a triclinic system with the $P\bar{1}$ space group. Concerning the molecular structure of the compound, the Hg(II) cation (d^{10}) with four sp^3 hybridized orbitals can form stable tetrahedral complexes with four coordinating atoms, because in the best structure of the diazoamino group ($-\text{N}=\text{N}-\text{N}<$), only the N(1) and N(3) atoms can be coordinated to the Hg(II) ion.^{4,5} Because of a large distance between the two methoxy groups and the angle strain, only one of the oxygen atoms can be coordinated to the Hg(II) cation; hence, the fourth necessary coordination will be provided by a chloride anion (Cl^-). The Hg and Cl atoms and the title ligand are disordered. Only one ("terminal") atom of the triazinide ligand (N-N-N) interact to Hg atoms (Hg(1)-N(1) and Hg(1A)-N(1A)). The Hg atoms of the second disordered position bonded to the other "terminal" N