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Crystal structure of dichlorido-(μ_2 -2,2'-(diazene-1,2-diyl)bis(benzen-1-ido)- κ^2 C:C')dimercury(II), $C_{12}H_8Cl_2Hg_2N_2$

Table 1: Data collection and handling.

Crystal:	Orange block
Size:	0.25 × 0.10 × 0.05 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	23.6 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	25.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	2145, 1160, 0.035
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1068
$N(\text{param})_{\text{refined}}$:	82
Programs:	Bruker [1], SHELX [2, 3]

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Abstract

$C_{12}H_8Cl_2Hg_2N_2$, triclinic, $P\bar{1}$ (no. 2), $a = 3.9815(8)$ Å, $b = 8.9837(18)$ Å, $c = 9.755(2)$ Å, $\alpha = 102.10(3)^\circ$, $\beta = 99.54(3)^\circ$, $\gamma = 98.82(3)^\circ$, $V = 329.98(12)$ Å³, $Z = 1$, $R_{\text{gt}}(F) = 0.0368$, $wR_{\text{ref}}(F^2) = 0.1061$, $T = 296(2)$ K.

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The title complex is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of 2,2'-azodibenzoic acid (6.8 mg, 0.025 mmol), NaOH (13.6 mg, 0.025 mol/L) and $HgCl_2$ (13.6 mg, 0.05 mmol) dissolved in CH_3OH (4 mL) were placed in a Teflon-lined stainless steel vessel, heated to 393 K for 3 days, and then cooled to room temperature over 24 h. Crystals of 1 were obtained.

Experimental details

The hydrogen atoms were placed in calculated positions and refined using a riding on attached atoms with isotropic

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Hg1	0.12404(9)	0.47083(5)	0.20380(3)	0.0343(2)
Cl1	−0.1617(8)	0.6634(4)	0.1469(3)	0.0444(7)
C1	0.529(3)	0.3114(13)	0.3996(11)	0.030(2)
C2	0.350(3)	0.2929(13)	0.2576(11)	0.030(2)
C3	0.332(3)	0.1536(14)	0.1617(11)	0.039(3)
H3	0.2196	0.1393	0.0670	0.046*
C4	0.474(3)	0.0356(14)	0.2017(12)	0.040(3)
H4	0.4562	−0.0568	0.1342	0.049*
C5	0.644(3)	0.0526(14)	0.3420(13)	0.041(3)
H5	0.7362	−0.0278	0.3703	0.050*
C6	0.672(3)	0.1934(14)	0.4384(12)	0.039(3)
H6	0.7908	0.2081	0.5322	0.047*
N1	0.566(2)	0.4459(11)	0.5149(8)	0.0322(19)

thermal parameters 1.2 times those of their carrier atoms. The U_{iso} values of the hydrogen atoms of methyl groups and oxygen were set to $1.5U_{\text{eq}}(\text{C}, \text{O})$.

Comment

Organomercurials rarely form isolable adducts with neutral or anionic nucleophiles [4]. However, in the solid state, the mercury center often engages in secondary weak interactions. Thus, inter- and intra-molecular Hg–O, Hg–N, Hg–S and Hg–X (X = halide) interactions are common occurrences in the solid state structures of organomercurials [5]. In these cases, these interactions usually lead to the formation of oligomers or even polymers in which the monomeric units

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can be connected by weak Hg···X (X = halide) interactions [6]. Meanwhile, azobenzene ligands have ability to form covalent bonds and other type of non-covalent interactions such as π - π and C—H··· π interactions due to the presence of p-conjugated system. Although their importance is well established for biological systems, there is a limited information on their role in organometallic compounds. Until now, some dimetalated complexes of azobenzene with metals such as Ni, Mn, Pd, and Ir have been reported [7–10]. An X-ray diffraction study of (phenylazophenyl-C,N')mercury(II) chloride had also been shown it to be dimeric *via* long Hg—Cl bridging interactions of 3.367 Å in the literature [11]. Here, we carried out the solvothermal reaction of 2,2'-azodibenzoic acid with Hg^{II} ion. In this case, the 2,2'-azodibenzoic acid/ 2,2'-azodibenzoate ligand was found to occur the decarboxylation of aromatic carboxylates leading to the simultaneous formation of deprotonated phenylazophenyl components. The title compound and the reported (phenylazophenyl-C,N')mercury(II) chloride in the literature [11] may be regarded as supramolecular structural isomers in which different space group and arrangement spatial are found. The asymmetric unit of the title structure is composed of one Hg^{II}, one half of a phenylazophenyl anion and one coordinated chloride. The decarboxylation cleavage reactions generated acute interest in the activation of C—Hg bonds. The Hg^{II} ion is bound to a chloride ion and a carbon atom. The Hg1—C and Hg1—Cl distances are 2.068(11) and 2.322(3) Å, respectively. In this structure a Hg—Cl contact of intermediate length (3.287 Å) is observed; as in the title compound, the Hg—N contact is weak, the distance being 2.710 Å.

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