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Supramolecular assemblages through metal-η^4-arene π-interactions: Synthesis and X-ray characterization of {Hg^{II}[NNN(PhR)$_2$]$_2$}$_n$ (R = NO$_2$, F), a bis diaryl-substituted triazenide complex polymer of Hg(II)

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Abstract

3-(2-fluorophenyl)-1-(3-nitrophenyl)triazene reacts with mercury(II) acetate in tetrahydrofuran in the presence of 2,2′-bipyridilamine to give yellow crystalline blocks of polymeric {Hg^{II}[NNN(PhR)$_2$]$_2$}$_n$ (R = NO$_2$, F). The new triazenide complex belongs to the triclinic space group $P\bar{1}$. In a molecule of {Hg^{II}[NNN(PhR)$_2$]$_2$} two deprotonated 1,3-diaryl-substituted triazenide ligands are coordinated in an opposite way to one Hg(II) ion by means of primary and secondary bonds. The Hg(II) ions are placed on the inversion centers of translation operated {Hg[NNN(PhR)$_2$]$_2$} moieties which are stacked along the crystallographic a-axis forming infinite unidimensional chains linked through metalocene alike Hg-η^2,η^2-arene π-interactions.
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1. Introduction

In a recent review, *Haiduc* and *Zukerman-Schpector* have shown that many reported organotellurium compounds, in addition to secondary Te$\cdots$halogen bonds, show also intermolecular bonds of the type Te$\cdots\pi$-aryl [1,2]. In early works, structural and crystallographic aspects of this complex type had been already shown [3–6], and, even if intermolecular interactions exist in almost all the reported cases, they have not been mentioned by the authors [7–10], specially the hydrogen bonds and the metal$\cdots\pi$-aryl interactions. This could be explained by the fact that only in recent years the real chemical meaning of the secondary bonds (or secondary interactions) has become clear. Fur-

thermore, several novel chemical concepts have been requested the development of target-orientated structure refinement programs, accomplished by the continual improvement of new X-ray diffractometers. This allows, among others evaluations, the localization of hydrogen atoms with relative accuracy, as well as the detection of weak intermolecular interactions. Thus, the updating of the analytical supplies has leaded to the fair introduction of a relative new chemical terminology. Later, several authors have extended the Haiduc-Zukerman's nomenclature describing, for example, self assembled supramolecular arrays through metal-π-C$_6$H$_5$ interactions [11,12] or super molecules with intra-chain metal$\cdots\pi$-aryl interactions [13,14], among other classifications, depending on the type of the molecular aggregate and the secondary interactions.

Triazenes and anionic triazenide ligands can show different types of coordination in metal complexes. They can be monodentate, (N1,N3)-chelating towards one metal atom or (N1,N3)-bridging over two metal atoms [15]. With the

aim, to extend the possibilities of coordination and to force close contacts between metal atoms, we have introduced *ortho*-, *meta*- and *para*-bis(phenyltriazene)benzenes (and substituted derivatives), with two triazene groups in one molecule as ligands, showing the metal complexes characterized so far, as expected, several different coordination types [16–19]. Hg(II) complexes of phenyltriazene chains are very rare, and the synthesis and characterization of $\{Hg[PhN_3C_6H_4N_3(H)Ph](NO_3)\}$ [20] was one of the few reports with evidence that in this complex type besides Metal–N bonds also metal–arene π-interactions play a significant role in the architecture of the crystalline lattice, in as much as the mentioned organotellurium compounds. With the purpose, to attain a supramolecular assembly of complex Hg(II)-phenyltriazenide molecules, we have extended the latter results to compounds including mono-catenated 1,3-diaryl-substituted triazenide ligands. We report now the synthesis and the X-ray characterization of polymeric $\{Hg[NNN(PhR)_2]_2\}_n$ (R = NO$_2$, F), a new triazenide complex of Hg(II) with metal-η^2,η^2-arene π-interactions, performed by coordinated (single) 1,3-diaryl-substituted triazenide chains. The Hg(II) ions represent the inversion center of quasi planar Hg(II)-bis 1,3-diaryl-substituted triazenide moieties which are disposed as unidimensional chains linked through metalocene alike Hg-η^2,η^2-arene π-interactions.

2. Experimental

2.1. $\{Hg[NNN(PhR)_2]_2\}_n$ (R = NO$_2$, F) trans-bis[3-(2-fluorophenyl)-1-(3-nitrophenyl)triazenide]mercury(II)

To a yellow pale solution prepared by dissolving 0.177 g (0.68 mmol) of 3-(2-fluorophenyl)-1-(3-nitrophenyl)triazene and 0.116 g (0,68 mmol) of 2,2′-bipyridilamine in 30 ml of tetrahydrofuran, 0.108 g (0.34 mmol) of mercury(II) acetate dissolved in 10 ml of methanol were added. After 2 h stirring a yellow precipitate was isolated by filtration. The vitric yellow solid was dried in the course of three weeks by slowly evaporation of the solvent giving yellow pale crystalline blocks.

Properties: air stable, crystalline substance. C$_{24}$H$_{16}$-F$_2$HgN$_8$O$_4$ (719.03); Yield: 0.059 g (0.082 mmol), 12.1% based on mercury(II) acetate. Melting point: 235–238 °C.

IR (KBr) *free ligand* 3-(2-fluorophenyl)-1-(3-nitrophenyl)triazene: 3301.59 (vs, v(N–H)), 1521.58 (vs, v_{as}(NO$_2$)), 1417.45 (s, v(N=N)), 1353.81 (s, v_s(NO$_2$)), 1268.95 (s, v(F–C$_{ar}$)), 1159.03 cm^{-1} (s, v_s(N–N)). $\{Hg[NNN(PhR)_2]_2\}_n$: the N–H band is suppressed. 1525.44 (vs, v_{as}(NO$_2$)), 1348.2 (vs, v_s(NO$_2$)), 1268.95 (s, v(F–C$_{ar}$)), 1232.31 cm^{-1} (s, v_{as}(NNN)), a mean value with respect to the N–N absorptions in the free ligand (average bond order).

2.2. Crystallography

X-ray data were collected with an Enraf–Nonius CAD-4 diffractometer. The structure of $\{Hg[NNN(PhR)_2]_2\}_n$

(R = NO$_2$, F) was solved by direct methods (SIR2002) [21]. Refinements were carried out with the SHELXL-97 [22] package. All refinements were made by full-matrix least-squares on F^2 with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were included in the refinement in calculated positions. Absorption correction was performed using the semi-empirical method Ψ scan [23].

3. Results and discussion

In the X-ray studies of triclinic $\{Hg[NNN(PhR)_2]_2\}_n$ (R = NO$_2$, F) the space group $P\bar{1}$ was solved on the basis of successful refinements. Crystal data and experimental conditions are given in Table 1. Selected bond distances and angles of the title complex are listed in Table 2; Fig. 1 displays the semi ORTEP [24] representation of monomer $\{Hg[NNN(PhR)_2]_2\}$ (R = NO$_2$, F), Fig. 2 shows two single, unidimensional, vicinal polymeric chains of the complex, parallel to the crystallographic direction [100], each of them linked through secondary metal-η^2,η^2-arene π-interactions (dashed lines).

In a molecule of the title complex two deprotonated 1, 3-diaryl-substituted triazenide ligands are coordinated in

Table 1
Crystal data and structure refinement for $\{Hg[NNN(PhR)_2]_2\}_n$ (R = NO$_2$, F)

Empirical formula	C$_{24}$H$_{16}$F$_2$HgN$_8$O$_4$
Formula weight	719.03
T (K)	293(2)
Radiation, λ (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	6.8318(10)
b (Å)	8.271(3)
c (Å)	11.3111(7)
α (°)	72.249(16)
β (°)	87.133(9)
γ (°)	79.979(17)
Volume (Å^3)	599.4(2)
Z, calculated density (g cm^{-3})	1, 1.992
Absorption coefficient (mm^{-1})	6.485
$F(000)$	346
Crystal size (mm)	0.36 × 0.33 × 0.20 mm
θ Range (°)	1.89–25.07
Index ranges	−8 ⩽ h ⩽ 8, −9 ⩽ k ⩽ 9, −13 ⩽ l ⩽ 0
Reflections collected	2249
Independent reflections [R_{int}]	2128 [0.0210]
Completeness to theta max (%)	100.0
Max. and min. transmission	0.3570 and 0.2036
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2128/0/179
Goodness-of-fit on F^2	1.084
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0258$, $wR_2 = 0.0636$
R indices (all data)	$R_1 = 0.0259$, $wR_2 = 0.0637$
Extinction coefficient	0.0022(11)
Largest difference in peak and hole (e Å^{-3})	1.344 and −2.187

Table 2
Selected bond lengths (Å) and angles (°) for $\{Hg[NNN(PhR)_2]_2\}_n$ (R = NO_2, F)

Bond lengths (Å)	
Hg–N(11)	2.077(4)
Hg···N(13)	2.768(3)
N11–N12	1.322(5)
N12–N13	1.276(5)
C(22)–F	1.345(6)
C(16)···F″	3.073(6)
Hg···C(25)′	3.152(5)
Hg···C(26)′	3.318(4)
Bond angles (°)	
N(11)″–Hg–N(11)	180.0(2)
N(11)″–Hg···N(13)	129.84(12)
N(11)–Hg···N(13)	50.16(12)
N(12)–N(11)–Hg	115.5(3)
C(11)–N(11)–Hg	126.2(3)
N(13)–N(12)–N(11)	111.4(3)
N(12)–N(13)–C(21)	113.4(3)
N(12)–N(13)···Hg	82.0(3)
C(21)–N(13)···Hg	163.6(3)
F–C(22)–C(23)	118.2(4)
F–C(22)–C(21)	119.0(4)
C25′···Hg···C26′	24.6(1)
Hg···C25′–C26′	84.4(3)
C25′–C26′···Hg	71.0(3)

Symmetry transformations used to generate equivalent atoms: (′) $1-x$, $1-y$, $-z$ and (″) $-x$, $1-y$, $-z$.

Fig. 2. The unit cell of $\{Hg[NNN(PhR)_2]_2\}$ (R = NO_2, F) with the unidimensional projection of a section of two centrosymmetric chains of the complex along the axis *a*. Dashed lines represent metal-η^2 secondary interactions. Symmetry transformations used to generate equivalent atoms: (′) $1-x$, $1-y$, $-z$.
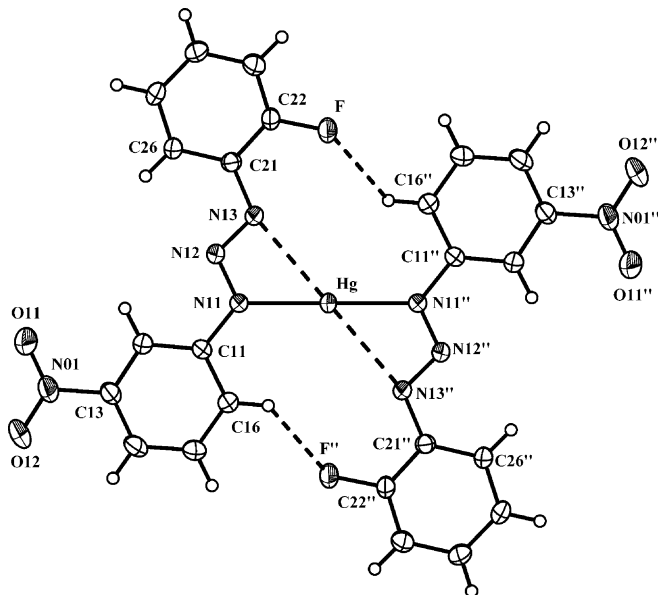

Fig. 1. Semi ORTEP [23] plot with atom-labeling scheme of the structure of monomer $\{Hg[NNN(PhR)_2]_2\}$ (R = NO_2, F); displacement ellipsoids at the 50% level. Dashed lines represent secondary interactions. Symmetry transformations used to generate equivalent atoms: (″) $-x$, $1-y$, $-z$.

an opposite way to one Hg(II) ion by means of two primary and four secondary (dashed lines) Hg–N and C–H···F interactions (see Fig. 1). The asymmetric unit is formally related with the other half of the molecule through a crystallographic inversion center, located on the Hg^{2+} ion.
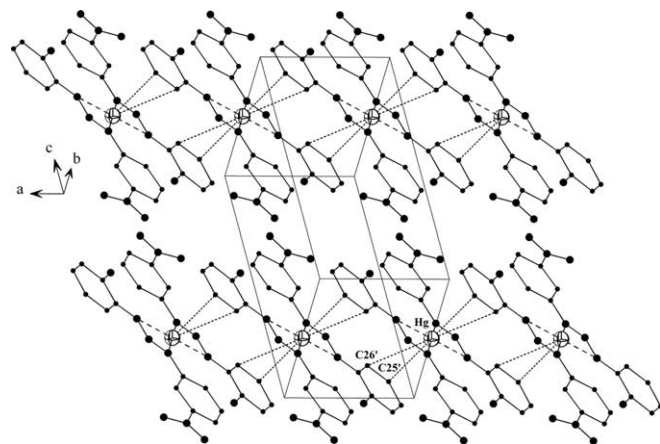
In the hitherto unknown structure of polymeric $\{Hg[NNN(PhR)_2]_2\}_n$ (R = NO_2, F), patent intermolecular interactions occur. The translation operated $\{Hg[NNN(PhR)_2]_2\}$ moieties are stacked along the crystallographic *a*-axis forming infinite chains. Each chain is related to the next one by a center of inversion. Within the chains each Hg^{2+} ion is additionally coordinated by two peripheral phenyl rings of two neighboring complexes (see Fig. 2). The two phenyl rings are located parallel to the main molecular plane and coordinate the Hg atom in a π type of bonding. In each single molecule the two fluorophenyl rings of the triazenide chains are linked toward two metallic centres, above and below the plane, reinforcing the chaining of the lattice. Thus, each $\{Hg[NNN(PhR)_2]_2\}$ moiety is linked with two other molecules through *four* secondary interactions of the type metal-η^2. These π interactions involve the Hg(II) ion and the atoms C25 {3.152(5)} and C26 {3.318(4) Å} as well as C25′ and C26′, generated by the symmetry transformation $1-x$, $1-y$, $-z$ (see Table 2). The distance from the metallic ion to the midpoint of the bonds C25′–C26′ is 3.24(3) Å, somewhat smaller than the distance of 3.38(3) Å observed to the mean Hg-η^2-arene π-interactions for the complex $\{Hg[PhN_3C_6H_4N_3(H)Ph](NO_3)\}$ [20]. Secondary Hg···N(13) {3.152(5) Å} and C–H···F interactions appear also within the "monomers" $\{Hg[NNN(PhR)_2]_2\}$, latter with distance of 3.073(6) Å (C16···F″) and angle of 129.31° {C16-H16···F″, symmetry code (″) $-x$, $1-y$, $-z$}. Although the η^2-arene distances Hg···C25 {3.152(5) Å} and Hg···C26 {3.318(4) Å} are quite short, there is a remarkable difference in the bond lengths from Hg to the other carbon atoms of the C21–C26 (and respective C21′–C26′) phenyl rings, as follows: Hg···C21 = 3.758(3), Hg···C22 = 3.983(3), Hg···C23 = 3.874(3) and Hg···C24 = 3.478(3) Å. This asymmetry of the Hg···C π interactions allow to exclude the possibility of occurrence of Hg···η^6-arene interactions, like the Te···π-aryl intermolecular bonds discussed earlier.

4. Supplementary material

Acknowledgements

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