

Note

Polymeric bidimensional self-assembling
of $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]$ ($\text{R} = m\text{-acetyl}$) through
metal- η^2, η^2 -arene π -interactions and non classical C–H \cdots O
bonding: Synthesis and X-ray characterization of a bis diaryl
symmetric-substituted triazenide complex of Hg(II)

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Abstract

Deprotonated 1,3-bis(3-acetylphenyl)triazene reacts with $\text{Hg}(\text{CH}_3\text{COO})_2$ and pyridine to give light-yellow crystals of $\{[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]\}_n$ ($\text{R} = \text{acetyl}$). The tectons $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]$ [$\text{R} = \text{CH}_3\text{C}(\text{O})$] are linked to pairs as centrosymmetric dimers through reciprocal metal- η^2 -arene π -interactions. The dimeric units are operated by a screw axis 2_1 parallel to the crystallographic direction $[010]$, also through a reflection–translation plane parallel to the c -axis, resulting a supramolecular bidimensional (2D) assembling of the dimeric tectons through non classical C–H \cdots (O)CCH₃ bonding.

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1. Introduction

At our days it is well known that selective, directional and strongly attractive noncovalent interactions can induce the self-assembly of predictable supramolecular aggregates. The molecules which play the role of building blocks in a self-assembled, ordered supramolecular structure are called *tectons* [1–3]. According to Simard and co-workers [2], a tecton (from Greek, *tekton*, builder) is defined as any molecule whose interactions are dominated by particular associative forces that induce the self-assem-

bly of an organized network with specific architectural or functional features. The design and construction of multi-component supermolecules or supramolecular arrays utilizing non-covalent bonding of tectons would be called *supramolecular synthesis* [3]. Thus, the supramolecular synthesis exploits successfully hydrogen-bonding and other types of non-covalent interaction, in building supramolecular systems [3–5].

Newly, we have shown that triazenide complexes of Hg(II) are tectons with a remarkably good ability to self-assemble through metal- η -arene π -interactions: the synthesis and characterization of $\{\text{Hg}[\text{PhN}_3\text{C}_6\text{H}_4\text{N}_3(\text{H})\text{Ph}](\text{NO}_3)\}$ [6] – a rare Hg(II) complex containing two phenyltriazene chains – is one of the few examples with evidence that besides the intramolecular metal–N bonds also intermolecular metal–arene π -interactions perform a significant

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role in the architecture of the crystal lattice. In $\{\text{Hg}[\text{PhN}_3\text{C}_6\text{H}_4\text{N}_3(\text{H})\text{Ph}](\text{NO}_3)\}$ the Hg(II) ions of the tectonic units are additionally coordinated by two peripheral phenyl rings of two neighboring complexes. The two phenyl rings are located parallel to the main molecular plane and coordinate the Hg(II) ion in a $\eta^2, \eta^2 \pi$ type of bonding. We have also successfully investigated the possibility to achieve a Hg- η^2 -arene dimerization by blocking one of the axial positions of the Hg(II) ion with pyridine [7]. In the complex $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R}')_2\text{Py}]_2$ ($\text{R} = \text{NO}_2$, $\text{R}' = \text{F}$), the tectons $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R}')_2\text{Py}]$ are linked in pairs as centrosymmetric dimers through reciprocal Hg- η^2 -arene secondary interactions. The dimeric units attain additionally intramolecular, secondary C-H...F interactions and are operated by translation in the crystallographic direction $[1\ 0\ 0]$, assembling unidimensional chains $\{[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R}')_2\text{Py}]_2\}_n$ linked through non classical C-H...O hydrogen bonds. In the elementary cell these chains are related in pairs through an inversion centre, without (extended) bidimensional interactions. The supramolecular synthesis of a tectonic bidimensional (2D) Hg(II)-triazenide self-assembling has been achieved with the preparation of polymeric $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R}')_2]_n$ [$\text{R} = \text{CH}_3\text{C}(\text{O})$, $\text{R}' = \text{F}$] [8], in which the Hg(II) ions represent the inversion centers of tectons comprised by planar Hg(II)-bis diaryl-substituted triazenide moieties, which are disposed as bidimensional chains, linked in one dimension through metallocene alike Hg- η^2, η^2 -arene π -interactions and in the second one through non classical C-H...O(CCH₃) hydrogen bonding. The above-mentioned compounds can be viewed as tectonic arrays assembled through intermolecular, secondary bonds which support the multiple stereochemistry requisites for a wide variety of structures, according to the necessity of self-assembling of their crystal lattices.

With the aim, to achieve a bidimensional, supramolecular assembling of *symmetrical* substituted triazenide chains, but starting from Hg- η^2 -arene dimers, we have optimized the synthesis of $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R}')_2\text{Py}]_2$ ($\text{R} = \text{NO}_2$, $\text{R}' = \text{F}$) [7] using 1,3-bis(3-acetylphenyl)triazene instead of asymmetrical substituted 1-(2-fluorophenyl)-3-(4-nitrophenyl)triazene. We report here on the synthesis and the X-ray characterization of bidimensional self-assembled $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]$ ($\text{R} = m$ -acetyl), a symmetric-substituted triazenide complex polymer of Hg(II). Characteristic for the new complex is the dimerization of the $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]$ tectons through reciprocal Hg- η^2 -arene secondary interactions and the expanding of the unidimensional, dimeric chains to a bidimensional arrangement through non classical C-H...O(CCH₃) interactions.

2. Experimental

All manipulations were carried out under nitrogen by use of standard Schlenk techniques.

2.1. $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]_2$ ($\text{R} = m$ -acetyl) bis{bis[1,3-bis(3-acetylphenyl) triazenide]pyridinyl-mercury(II)}

Small scrapings of metallic sodium were added under stirring to a solution of 0.084 g (0.30 mmol) of 1,3-bis(3-acetylphenyl)triazene in 10 ml of anhydrous acetone. To the yellow solution of the deprotonated ligand 0.048 g (0.15 mmol) of $\text{Hg}(\text{CH}_3\text{COO})_2$ dissolved in 5 ml of absolute methanol was added. After 24 h stirring, 2 g of anhydrous magnesium sulfate is added and the mixture is stirred further during 1/2 h. The mixture was filtered and the solvent was evaporated. The residual yellow solid was dissolved in an absolute mixture of tetrahydrofuran (10 ml)/pyridine (3 ml). Prismatic light-yellow crystals were obtained after slow evaporation of the solvent at room temperature within two weeks.

Properties: prismatic light-yellow crystalline substance. $\text{C}_{37}\text{H}_{33}\text{HgN}_7\text{O}_4$ (840.29). Yield: 0.041 g (0.049 mmol), 33% based on $\text{Hg}(\text{CH}_3\text{COO})_2$. Melting point: 204–206 °C.

IR (KBr) *free ligand* 1,3-bis(3-acetylphenyl)triazene: 3253 [s, $\nu(\text{N-H})$], 1682 [vs, $\nu(\text{C=O})$], 1530 [vs, $\nu(\text{C-O})$], 1402 [m, $\nu(\text{N=N})$], 1192 cm^{-1} [s, $\nu_s(\text{N-N})$].

$[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]_2$ [$\text{R} = \text{CH}_3\text{C}(\text{O})$]: the $\nu\text{N-H}$ band is absent.

2.2. Crystallography

Data were collected with a Bruker APEX II CCD diffractometer and graphite-monochromatized Mo $K\alpha$ radiation. The data reduction and the absorption correction were performed using SAINT [9] and SADABS [10] programs, respectively. The structure of $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]_2$ ($\text{R} = m$ -acetyl) was solved by direct methods [11] and refined on F^2 with anisotropic temperature parameters for all non H atoms [12]. H atoms of the phenyl and methyl groups were positioned geometrically ($\text{C-H} = 0.93 \text{ \AA}$ for Csp^2 and 0.97 \AA for Csp^3 atoms) and treated as riding on their respective C atoms, with $U_{\text{iso}}(\text{H})$ values set at $1.2U_{\text{eq}}\text{Csp}^2$ and $1.5U_{\text{eq}}\text{Csp}^3$. The crystallographic parameters and details of data collection and refinement are given in Table 1.

3. Results and discussion

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 shows the molecular structure of the tecton $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]$ [$\text{R} = \text{CH}_3\text{C}(\text{O})$] in a thermal ellipsoid representation [13], Fig. 2 shows a section of the polymeric bidimensional lattice, linked through secondary metal- η^2, η^2 -arene π -interactions and C-H...O bonding (dashed lines).

In a single tecton $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]$ [$\text{R} = \text{CH}_3\text{C}(\text{O})$] the Hg(II) centre is planar coordinated by two triazenide ions through two primary Hg-N bonds [$\text{Hg-N}(11) = 2.102(5)$, $\text{Hg-N}(21) = 2.107(6) \text{ \AA}$] and two

Table 1
Crystal data and structure refinement for $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]$
(R = *m*-acetyl)

Empirical formula	$\text{C}_{37}\text{H}_{33}\text{HgN}_7\text{O}_4$
Formula weight	840.29
<i>T</i> (K)	293(2)
Radiation, λ (Å)	0.71073
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	
<i>a</i> (Å)	13.8647(5)
<i>b</i> (Å)	14.8823(5)
<i>c</i> (Å)	17.0403(5)
α (°)	90
β (°)	92.2140(10)
γ (°)	90
Volume (Å ³)	3513.4(2)
<i>Z</i> , calculated density (g cm ⁻³)	4, 1.589
Absorption coefficient (mm ⁻¹)	4.430
<i>F</i> (000)	1664
Crystal size (mm)	0.27 × 0.23 × 0.17
θ Range (°)	1.47–25.50
Index ranges	$-13 \leq h \leq 16$, $-16 \leq k \leq 18$, $-20 \leq l \leq 20$
Reflections collected	33 113
Independent reflections	6407 [$R_{\text{int}} = 0.0258$]
Completeness to θ max.	98.0%
Maximum and minimum transmission	0.5197 and 0.3809
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6407/0/443
Goodness-of-fit on F^2	1.160
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0440$, $wR_2 = 0.1034$
<i>R</i> indices (all data)	$R_1 = 0.0639$, $wR_2 = 0.1381$
Extinction coefficient	0.0059(4)
Largest difference peak and hole (e Å ⁻³)	1.711 and -1.632

Table 2
Selected bond lengths [Å] and angles [°] for $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]$
(R = *m*-acetyl)

Bond lengths		Bond angles	
Hg–N(11)	2.102(5)	N(11)–Hg–N(21)	174.53(18)
Hg–N(21)	2.107(6)	N(11)–Hg–N(51)	93.87(15)
Hg–N(51)	2.521(5)	N(21)–Hg–N(51)	91.51(15)
Hg...N(13)	2.693(5)	N(11)–Hg...N(13)	51.23(17)
Hg...N(23)	2.716(6)	N(21)–Hg...N(13)	129.68(18)
Hg...C(16)′	3.487(6)	N(21)–Hg...N(23)	50.66(19)
Hg...C(15)′	3.574(7)	N(13)...Hg...N(23)	178.25(15)
C(56)′...O(4)′′	3.078(8)	N(11)–Hg...C(16)′	70.89(18)
C(56)–H(56)	0.9300	N(21)–Hg...C(16)′	103.69(18)
N(13)–N(12)	1.290(7)	N(11)–Hg...C(15)′	83.93(19)
N(11)–N(12)	1.326(7)	N(21)–Hg...C(15)′	91.15(19)
N(22)–N(23)	1.267(8)	C(16)′...Hg...C(15)′	22.33(17)
N(22)–N(21)	1.320(7)	N(22)–N(21)–Hg	113.1(4)
		C(31)–N(21)–Hg	129.0(4)
		N(22)–N(23)–Hg	84.8(4)

Symmetry transformations used to generate equivalent atoms: (′) $-x, -y + 1, -z$; (′′) $x, -y + 3/2, z - 1/2$.

secondary ones [Hg...N(13) = 2.693(5), Hg...N(23) = 2.716(6) Å]. The square pyramidal configuration of $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]$ is achieved with a neutral

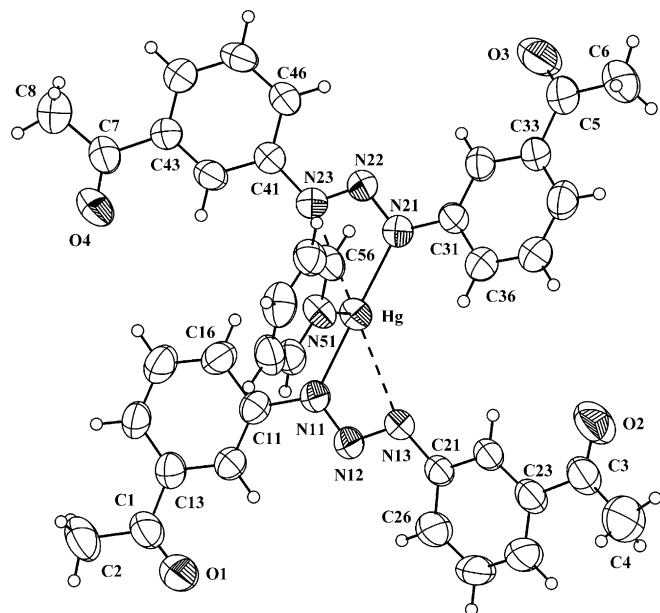


Fig. 1. The molecular structure with atom-labeling scheme of the tecton $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]$ [R = $\text{CH}_3\text{C}(\text{O})$] [13]. Displacement ellipsoids at the 50% level. Dashed lines represent secondary interactions. Symmetry transformations used to generate equivalent atoms: (′) $-x, -y + 1, -z$.

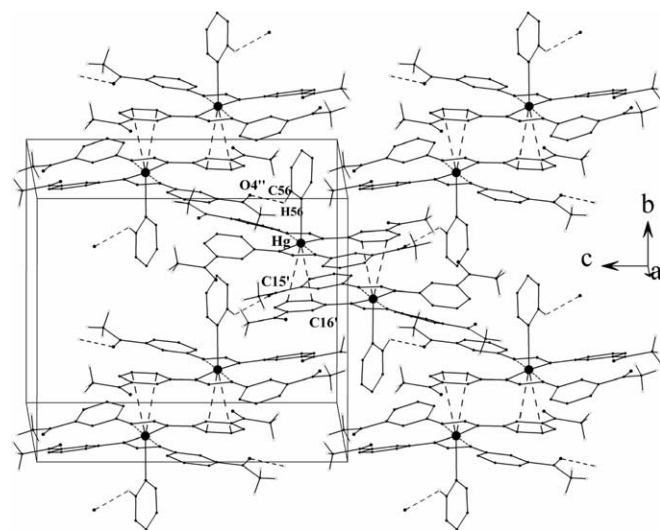


Fig. 2. Section of the supramolecular, bidimensional (2D) assembling of $\{[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]_n\}_n$ [R = $\text{CH}_3\text{C}(\text{O})$], showing five dimeric moieties. Intermolecular, centrosymmetric Hg- η^2, η^2 -arene π -interactions (along the *b*-axis) and non-classical C–H...O bonding (*c*-axis) in dashed lines. Symmetry transformations used to generate equivalent atoms: (′) $-x, -y + 1, -z$; (′′) $x, -y + 3/2, z - 1/2$.

pyridine ligand in the apical position [Hg–N(51) = 2.521(5) Å]. The Hg(II) ion is 0.069(2) Å out of the plane settled by the four coordinating nitrogen atoms. The pyridine ring attains with this plane an angle of 89.5(1)°. This small deviation of the ideal interplanar angle (90°) can be justified because of the non classical C–H...O)CCH₃

(hydrogen) bonding of the lattice, involving the *ortho* C–H group of the pyridine ring. The tectons $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNN}-\text{C}_6\text{H}_4\text{R})_2\text{Py}]$ [$\text{R} = \text{CH}_3\text{C}(\text{O})$] are linked to pairs as centrosymmetric dimers through reciprocal Hg–arene secondary interactions. The dimeric units are operated by a screw axis 2_1 parallel to the crystallographic direction $[0\ 1\ 0]$, also through a reflection–translation plane parallel to the *c*-axis, resulting a supramolecular bidimensional (2D) assembling of the dimeric tectons through the above mentioned non classical C–H \cdots (O)CCH₃ bonding $[\text{C}(56)\cdots\text{O}(4)'' = 3.078(8)\ \text{\AA}$, $\text{C}(56)\text{--H}(56)\cdots\text{O}4'' = 125.03^\circ$, symmetry code ($''$) $x, 3/2 - y, 1/2 + z$].

Fig. 2 shows the bidimensional crystal lattice of five dimeric tectons $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]_2$ linked through the C–H \cdots (O)CCH₃ secondary bonds in the *bc*-plane. The bonding phenyl rings are oriented parallel to the main molecular plane and coordinate the Hg atom in a π type of bonding. Two carbon atoms of the phenyl rings have remarkably short distances to the Hg(II) ion: these shorter secondary interactions are of 3.487(6) [Hg \cdots C(16)'] and 3.574(7) Å [Hg \cdots C(15)'], symmetry code ($'$) $-x, -y + 1, -z$. The distance of the π -interaction from Hg to the midpoint of the C(15)–C(16)' bond is 3.51 Å, somewhat larger than the distance from the metallic ion to the midpoint of the C(31)^I–C(36)^I bond [3.38 Å, symmetry code (^I) $x, y - 1, z$] in {Hg[PhN₃C₆H₄N₃(H)Ph](NO₃)} [6], but identical to the midpoint distance C(34)'–C(35)' [symmetry code ($'$) $-x + 1, -y, -z$] in the complex $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R}')_2\text{Py}]_2$ ($\text{R} = \text{NO}_2, \text{R}' = \text{F}$) [7].

The angles C–Hg–C of the metal–arene π interactions are 22.33(17)° [C(16)' \cdots Hg \cdots C(15)'], 75.3(4)° [Hg \cdots C(15)'–C(16)'] and 82.4(4)° [C(15)'–C(16)' \cdots Hg], fairly close to the angles [22.5(1)° (C34' \cdots Hg \cdots C35'), 74.3(3)° (Hg \cdots C34'–C35'), 83.3(3)° (C34'–C35' \cdots Hg)] found in $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R}')_2\text{Py}]_2$ ($\text{R} = \text{NO}_2, \text{R}' = \text{F}$) [7].

As a conclusion, and like the other mentioned examples, the asymmetry of the Hg \cdots C π contacts in $[\text{Hg}^{\text{II}}(\text{RC}_6\text{H}_4\text{NNNC}_6\text{H}_4\text{R})_2\text{Py}]$ [$\text{R} = \text{CH}_3\text{C}(\text{O})$] allows to exclude the possibility of occurrence of intermolecular interactions of the type Hg– η^6 -arene.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC No. 290251. Further details of the crystal structures investigations are available free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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