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Unidimensional Self-assembling of $\{Hg^{II}[NNN(PhBr)_2]_2\}$ through Metal-η^4-arene π-Interactions: Synthesis and X-Ray Characterization of a Bis Diaryl Symmetric-substituted Triazenide Complex Polymer of Mercury(II)

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Abstract. A solution of deprotonated 1,3-bis(4-bromophenyl)triazene reacts with $Hg(CH_3COO)_2$ in methanol / tetrahydrofurane to give yellow crystalline needles of $\{Hg^{II}[NNN(PhBr)_2]_2\}_n$, a triazenide complex polymer of Hg^{II} with metal-η^2,η^2-arene π-interactions, performed by coordinated single triazenide chains. The crystal structure of the new polymeric complex of Hg^{II} belongs to the monoclinic space group $P2_1/n$. The lattice of $[Hg^{II}(BrPhNNNPhBr)_2]_n$ can be viewed as a one-dimensional assembling of planar tectons $[Hg^{II}(BrPhNNNPhBr)_2]$ linked through metalocene alike Hg^{II}-η^2,η^2-arene π-interactions along the crystallographic *b* axis.

Keywords: Mercury; Triazenes; Triazenide complexes; Supramolecular assembling; π-Interactions

Introduction

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 *M. 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-assembly of an organized network with specific architectural or functional features. The design and construction of multicomponent 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 Mercury(II) are tectons with a remarkably good ability to self-assemble of different manners through metal-η-arene π-interactions: the synthesis of $\{Hg[PhN_3C_6H_4N_3(H)Ph](NO_3)\}$ [6] − a rare Mercury(II) complex containing two phenyltriazenide chains − was one of the first evidences that in this complex type besides Metal-N bonds also metal-arene π-interactions perform a significant role in the architecture (or self-assembling) of the crystalline lattice. In this complex 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 η^2,η^2 π type of bonding.

More recently we have described [7] the synthesis of polymeric $\{Hg[NNN(PhR)_2]_2\}_n$ (R $=NO_2$, F), a new triazenide complex of Mercury(II) with metal-arene π-interactions, performed by coordinated (single) 1,3-diaryl-substituted triazenide chains. In a tectonic molecule of $\{Hg^{II}[NNN(PhR)_2]_2\}$ two deprotonated asymmetric 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 $\{Hg[NNN(PhR)_2]_2\}$ tectons which are stacked along the crystallographic *a* axis forming infinite unidimensional chains linked through metalocene alike Hg-η^2,η^2-arene π-interactions. Secondary Hg···N and C−H···F interactions appear also within the tectons $\{Hg[NNN(PhR)_2]_2\}$. In the reported compound [7] only the planar coordination sites of the metal ion were compromised, the two axial π-interacting positions were free.

The possibility to achieve a Hg-η^2-arene dimerization by blocking one of the axial positions of the Hg^{II} ion with pyridine was also successfully investigated [8]. In the new complex $[Hg^{II}(RPhNNNPhR')_2Py]_2$ (R = NO_2, R′ = F), the tectons $[Hg^{II}(RPhNNNPhR')_2Py]$ 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 [100], assembling unidimensional chains $\{[Hg^{II}(RPhNNNPhR')_2Py]_2\}_n$ linked through non classical C−H···O hydrogen bonds. In the unit cell these chains are related in pairs through an inversion centre, without bidimensional interactions.

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Giving sequence to our experiments involving the supramolecular syntheses of tectonic unidimensional Hg-triazenide chains, we report now on the synthesis and the X-ray characterization of a symmetric-substituted triazenide complex polymer of Hg^{II} with metal-η^2,η^2-arene π-interactions, performed by coordinated (single) triazenide chains. In the title compound $\{Hg^{II}[NNN(PhBr)_2]_2\}_n$ the Hg^{II} ions represent the inversion center of tectons comprised by 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.

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; Figure 1 shows the molecular structure ofthe tecton $\{Hg[NNN(PhBr)_2]_2\}$ in a thermal ellipsoid representation [9], Figure 2 shows a section of the polymeric unidimensional lattice, linked through secondary metal-η^2,η^2-arene π-interactions (dashed lines).

In a single tecton $\{Hg[NNN(PhBr)_2]_2\}$ two deprotonated symmetric 1,3-bis(4-bromophenyl)triazenide ligands are coordinated to one Hg^{II} ion by means of two primary Hg−N bonds and two secondary Hg−N interactions (dashed lines, 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. The complex $\{Hg[NNN(PhBr)_2]_2\}$ is essentially planar. The Hg^{II} ion, all the six triazenide N atoms and the terminal C(11)−C(16)Br(1) aryl ring, generate a plane with a maximum deviation from coplanarity of 0.0364 Å. The second terminal aryl ring [C(21)−C(26)Br(2)] exhibits an appreciable deviation [10.9(2)°] from this plane. The linear coordination of the Hg^{2+} ion is achieved by two triazenide anions through N(11,11′) [Hg−N(11) = 2.061(4) Å] and the weak interactions Hg···N(13, 13′) with a distance of 2.771(5) Å. These Hg−N and Hg···N distances are similar to the corresponding bond lengths in the triazenide complex $\{Hg^{II}[NNN(PhR)_2]_2\}_n$ (R = NO_2, F) [7], Hg−N(11) = 2.077(4) and Hg···N(13) = 2.768(3) Å.

Table 1 Crystal data and structure refinement for $\{Hg^{II}[NNN(PhBr)_2]_2\}$

Empirical formula	$C_{24}H_{16}Br_4HgN_6$
Formula weight	908.66
T /K	293(2)
Radiation, *λ* /Å	0.71073
Crystal system, space group	monoclinic,$P2_1/n$
Unit cell dimensions, *a*, *b*, *c* /Å	*a* = 15.1741(6), *b* = 4.6587(2), *c* = 18.5342(7) *β* = 94.207(2)°
Volume /Å	1306.68(9)
Z, Calculated Density /g.cm^{-3}	2, 2.309
Absorption coefficient /mm^{-1}	12.031
F(000)	844
Crystal size /mm	0.38 x 0.10 x 0.09
Theta range /°	1.68 − 25.50°
Index ranges	$-18 \leq h \leq 18$, $-5 \leq k \leq 5$, $-22 \leq l \leq 22$
Reflections collected	18442
Independent reflections	2433 [R_{int} = 0.0322]
Completeness to theta max.	100.0 %
Max. and min. transmission	0.4106 and 0.0918
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2433 / 0 / 160
Goodness-of-fit on F^2	1.343
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0278$, $wR_2 = 0.0798$
R indices (all data)	$R_1 = 0.0386$, $wR_2 = 0.1119$
Largest diff. peak and hole /e·Å^{-3}	1.265 and −0.925

In the hitherto unknown structure of the polymeric title complex intermolecular interactions are patent. The translation operated moieties are stacked unidimensionally along the crystallographic *b* axis through Hg-η^2,η^2-arene π-interactions between the Hg^{II} ion and carbon atoms of two peripheral phenyl rings of two neighboring complexes. In the unit cell packing the single chains are related through 2_1 screw axes parallel to the *b* axis. The tectonic moieties $\{Hg[NNN(PhBr)_2]_2\}$ attain furthermore intramolecular, secondary Hg···N interactions (see Table 2 and Fig. 1), also accountable for the planarity of the tectons. The two phenyl rings of the metalocene alike Hg-η^2,η^2-arene π-interactions are located parallel to the main molecular plane of the tectons $[Hg^{II}(RPhNNNPhR')_2]$ and coordinate the Hg^{II} ions in a π type of bonding. In each single molecule the two bromophenyl rings of the triazenide chains are linked toward two metallic centres, above and below the plane, reinforcing the chaining of the lattice. Thus, each tecton $[Hg^{II}(BrPhNNNPhBr)_2]$ is linked with two other ones through *four* secondary interactions of the metal-η^2 type. Two carbon atoms of the C21−C26 ring have remarkably short distances to the Hg^{II} ion: these shortest intermolecular distances from the Hg^{II} centres toward the phenyl rings are 3.297(6) [Hg(1)···C(21)″] and 3.429(6) Å [Hg(1)···C(22)″, symmetry code (″) *x*, *y*+1, *z*]. The distance from the metallic ion to the midpoint of the C(21)″−C(22)″ bond is 3.36 Å, smaller than the midpoint distances C(31^I)−C(36^I) [3.38 Å, symmetry code (′) *x*, *y*−1, *z*] and C34′−C35′ [3.51 Å, symmetry code (′) −*x*+1, −*y*, −*z*] in the complexes $\{Hg[PhN_3C_6H_4N_3(H)Ph](NO_3)\}$ [6] and $[Hg^{II}(RPhNNNPhR')_2Py]_2$ (R = NO_2, R′ = F)[8] respectively, but larger than the distance from the metallic ion to the midpoint

Table 2 Selected bond lengths /Å and angles /° for $\{Hg^{II}[NNN(PhBr)_2]_2\}$

Bond lengths			
C(14)−Br(1)	1.894(6)	N(13)−N(12)−N(11)	111.9(5)
C(24)−Br(2)	1.896(7)	N(12)−N(13)−C(21)	113.5(5)
N(11)−N(12)	1.324(7)	N(11)′−Hg(1)−N(11)	180.0(2)
N(11)−Hg(1)	2.061(4)	N(11)′−Hg(1)···N(13)′	50.5(2)
N(12)−N(13)	1.280(7)	N(11)−Hg(1)···N(13)′	129.5(2)
Hg(1)···N(13)′	2.771(5)	N(11)′−Hg(1)···C(21)″	99.8(2)
Hg(1)···C(21)″	3.297(6)	N(11)−Hg(1)···C(21)″	80.2(2)
Hg(1)···C(22)″	3.429(6)	N(13)′···Hg(1)···C(21)″	102.0(1)
Bond angles		N(11)′−Hg(1)···C(22)″	84.9(2)
N(12)−N(11)−C(11)	117.7(4)	N(11)−Hg(1)···C(22)″	95.1(2)
N(12)−N(11)−Hg(1)	115.4(3)	N(13)′···Hg(1)···C(22)″	106.4(2)
C(11)−N(11)−Hg(1)	126.8(4)	C(21)″···Hg(1)···C(22)″	23.8(1)

Symmetry transformations used to generate equivalent atoms: (′) −*x*+2, −*y*+2, −*z*; (″) *x*, *y*+1, *z*.

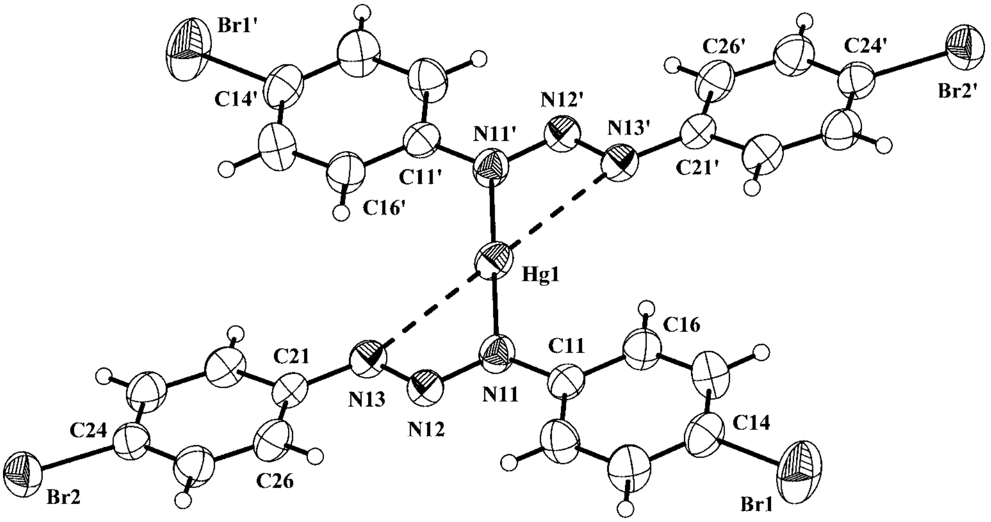

Fig. 1 The molecular structure with atom-labeling scheme of the tecton $[Hg^{II}(BrPhNNNPhBr)_2]$ [9]. Displacement ellipsoids at the 50 % level. Dashed lines represent secondary interactions. Symmetry transformations used to generate equivalent atoms: (′) $-x+2$, $-y+2$, $-z$.

of the C25′−C26′ bond [3.24(3) Å, symmetry code (′) $1-x$, $1-y$, $-z$] in $\{Hg[NNN(PhR)_2]_2\}_n$ (R = NO_2, F) [7]. The angles of the metal-arene π interactions are 23.8(1)° [C(21)″···Hg(1)···C(22)″], 83.4(4)° [Hg(1)···C(21)″−C(22)″] and 72.8(3)° [C(21)″−C(22)″···Hg(1)], fairly close to the angles found in $[Hg^{II}(RPhNNNPhR')_2Py]_2$ (R = NO_2, R′ = F) [8] [C34′···Hg···C35′ = 22.5(1)°, Hg···C34′−C35′ = 74.3(3)°, C34′−C35′···Hg = 83.3(3)°; symmetry code (′) $-x+1$, $-y$, $-z$], $\{Hg[PhN_3C_6H_4N_3(H)Ph](NO_3)\}$ [6] [$C31^I$···Hg···$C36^I$ = 23(3)°, Hg···$C31^I-C36^I$ = 79(8)°, $C31^I-C36^I$···Hg = 78(7)°; symmetry code (′) x, $y-1$, z] and $\{Hg[NNN(PhR)_2]_2\}_n$ (R = NO_2, F) [7] [C25′···Hg···C26′ = 24.6(1)°, Hg···C25′−C26′ = 84.4(3), C25′−C26′···Hg = 71.0(3)°; symmetry code (′) $1-x$, $1-y$, $-z$]. Since no other interactions besides Hg···π contacts exist, the tectonic unidimensional chains can not extend to a supramolecular bidimensional (2D) assembling. Finally, and like the above mentioned examples, the asymmetry of the Hg···Ph π contacts in $[Hg^{II}(BrPhNNNPhBr)_2]_n$ allows to exclude the possibility of occurrence of intermolecular interactions of the type Hg−-η^6-arene.

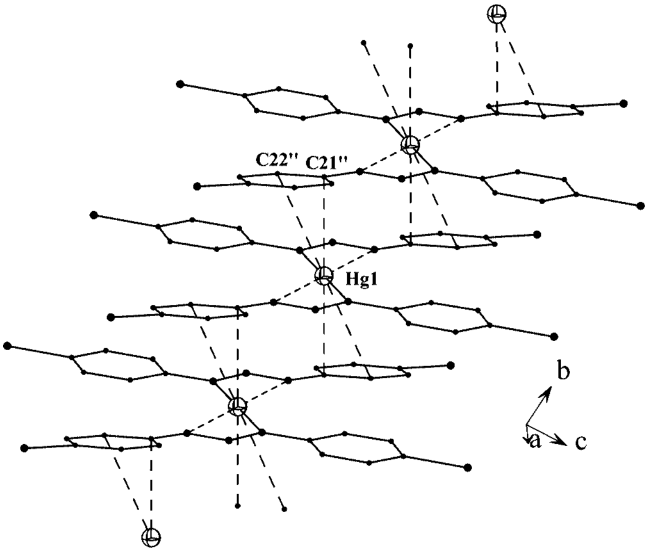

Fig. 2 Section of the supramolecular, unidimensional assembling of $[Hg^{II}(BrPhNNNPhBr)_2]_n$. Intermolecular, centrosymmetric Hg-η^2,η^2-arene π-interactions (along the *a* axis) in dashed lines. Symmetry transformations used to generate equivalent atoms: (″) x, $y+1$, z.

Experimental Section

A single crystal fixed on a glass fiber was used for the X-ray data collection. Data were collected with a Bruker APEX II CCD area-detector diffractometer and graphite-monochromatized Mo-K_α radiation. The data reduction and the absorption correction were performed using *SAINT* [10] and *SADABS* [11] programs, respectively. The structure of $\{Hg^{II}[NNN(PhBr)_2]_2\}$ was solved by direct methods [12] and refined on F^2 with anisotropic temperature parameters for all non H atoms [13]. H atoms of the phenyl groups were positioned geometrically (C−H = 0.93 Å for Csp^2 atoms) and treated as riding on their respective C atoms, with U_{iso}(H) values set at $1.2U_{eq}Csp^2$. The crystallographic parameters and details of data collection and refinement are given in Table 1.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC no. 288836. 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**).

Preparation of $\{Hg[NNN(PhBr)_2]_2\}_n$ trans-bis[1,3-(4-bromophenyl)triazenide] mercury(II)

To a solution of 0.050 g (0.14 mmol) of 1,3-bis(4-bromophenil)triazene in 15 ml of pure acetone three drops of a methanolic solution of KOH (0.1 %) were added. The addition of 0.022 g (0.070 mmol) of $Hg(CH_3COO)_2$ dissolved in 5 ml of pure methanol and 1 ml of pyridine to the deprotonated light-orange mixture turned the color yellow. After 24 h stirring the solvent was slowly evaporated. An yellow solid was dissolved in 20 ml of pure tetrahydrofuran. The evaporation of the solvent within 10 days at room temperature gives light yellow crystalline needles suitable for X-ray analysis.

Properties: vitreous, crystalline light-yellow needles. $C_{24}H_{16}Br_4HgN_6$ (908.66). Yield: 0.022 g (0.024 mmol), 35 % based on $Hg(CH_3COO)_2$. Melting point: 235−238 °C.

IR (KBr) *free ligand* 1,3-(4-bromophenyl)triazene: 3195 (vs, ν(N−H)), 1395 (m, ν_{as}(N=N)), 1248 (s, ν_s(N−N)), 1071 cm^{-1} (vs, ν(Br−C_{ar})).

[$Hg^{II}(RPhNNNPhR)_2$] [R = Br]: the N−H band is absent. 1329 cm^{-1} (s, ν_{as}(NNN)), a mean value with respect to the N-N absorptions in the free ligand (average bond order), 1069 cm^{-1} (s, ν(Br−C_{ar})). FIR (CsI): 579 cm^{-1} (s, ν(Hg−N)).

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