

Polymeric assembling through reciprocal metal- η^2 -arene π -interactions: Synthesis and X-ray characterization of $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]_2$ ($\text{R} = \text{NO}_2$, $\text{R}' = \text{F}$), an asymmetric bis diaryl-substituted triazenide–pyridinyl complex of Hg(II)

Manfredo Hörner^{a,*}, Gelson Manzoni de Oliveira^{a,*}, Jeferson André Naue^a,
Jörg Daniels^b, Johannes Beck^b

^a Departamento de Química, Universidade Federal de Santa Maria, 97105–900 Santa Maria, RS, Brazil

^b Institut für Anorganische Chemie der Rheinischen Friedrich-Wilhelms-Universität, Gerhard-Domagk-Straße 1, D-53121 Bonn, Germany

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Abstract

$\text{Hg}(\text{SCN})_2$ reacts with 3-(2-fluorophenyl)-1-(4-nitrophenyl)triazene in tetrahydrofuran in the presence of triethylamine to give orange crystals of $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]_2$ ($\text{R} = \text{NO}_2$, $\text{R}' = \text{F}$), a new polymeric triazenide–pyridinyl complex of Hg(II) with reciprocal metal- η^2 -arene π -interactions. The crystal structure belongs to the triclinic space group $P\bar{1}$, and the lattice of $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]_2$ can be viewed as a supramolecular unidimensional assembling of tectonic $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]$ units linked through intermolecular metal-arene π interactions and non-classical C–H...O hydrogen bonding.

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1. Introduction

In the present days it is well known that secondary bonds, or interactions, can play a significant role in the structural assembling of a wide variety of compounds. These interactions present σ or π character, and have not been recognized in earlier works, in spite of their real existence. Organotellurium compounds, for example, in addition to secondary Te...halogen bonds, show mostly intermolecular bonds of the type Te... π -aryl [1,2]. In former works structural and crystallographic aspects of this complex type had been already shown, and, even if intermolecular interactions exist in almost all the reported cases, they have not been mentioned by the authors [3–6], spe-

cially the hydrogen bonds and the metal... π -aryl interactions. This could be explained by the fact that only in recent years the real chemical significance of the secondary bonds (or secondary interactions) has become evident. Furthermore, several novel chemical concepts have been requested the development of target-orientated structure refinement programs, accomplished by the continual improvement of new X-ray diffractometric devices. This allows, among others evaluations, the localization of hydrogen atoms with relatively high accuracy, as well as the detection of weak intra- and intermolecular interactions. Thus, the progress of the analytical supplies has led to the fair introduction of a relative new chemical terminology.

This new or alternative nomenclature has been foremost introduced to describe structural aspects of organochalcogenes, a kind of compounds which overpass simple description so that concepts like hypervalence, multicenter

* Corresponding authors. Tel.: +55 55 3220 8056; fax: +55 55 3220 8031.
E-mail addresses: hoerner@smail.ufsm.br (M. Hörner), manzoni@quimica.ufsm.br (G.M. de Oliveira).

bonding, charge transfer interactions, secondary bonding, have been introduced for the understanding of their structural and chemical properties [7,8]. Moreover, several authors have extended the Haiduc-Zuckerman's archetype "supramolecular self assembly" [1,2], describing, for example, self assembled supramolecular arrays through metal- π -C₆H₅ interactions [9,10] or super molecules formed through Te...X secondary bonds with intra-chain Te... π -aryl interactions [11,12], among other classifications, depending on the type of the molecular aggregate and secondary interactions.

Secondary bonding can also lead to the polymerization and oligomerization of different organometallic compounds, although this effect was first assigned to describe the chemistry of organylchalcogenes. The synthesis and characterization of {Hg[PhN₃C₆H₄N₃(H)Ph](NO₃)} [13] – a very 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 role in the architecture of the crystal lattice, in as much as the mentioned organotellurium compounds. Recently, we have described [14] the synthesis of polymeric {Hg[NNN(PhR)₂]₂}_n (R = NO₂, 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 translation operated {Hg[NNN(PhR)₂]₂} moieties are stacked along the crystallographic *a* axis to infinite chains. Each chain is related to the next one by a center of inversion. Within the chains each Hg²⁺ ion is 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 atom through metallocene alike Hg- η^2 , η^2 -arene π -interactions. In the reported compound [14] 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 -arene dimerization by blocking one of the axial positions of the Hg(II) ion with pyridine was successfully investigated. We report here on the synthesis and the X-ray characterization of [Hg^{II}(RPhNNNPhR')₂Py]₂ (R = NO₂, R' = F), a new polymeric triazenide complex of Hg(II) with reciprocal metal- η^2 -arene π -interactions, performed by coordinated asymmetric 1,3-diaryl-substituted triazenide chains. The coordination at Hg(II) is square pyramidal, with primary and secondary Hg–N bonds in the basal positions and the pyridine ligand in the apical position. In the whole lattice the Hg ions achieve and octahedral coordination through dimerization by means of reciprocal metal- η^2 -arene π -interactions with the phenyl groups of neighbored complexes.

2. Experimental

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

2.1. [Hg^{II}(RPhNNNPhR')₂Py]₂ (R = NO₂, R' = F) bis{trans-bis[3-(2-fluorophenyl)-1-(4-nitrophenyl)triazene]pyridinyl-mercury(II)}

A mixture of 0.5 ml of triethylamine and 0.101 g (0.32 mmol) of Hg(SCN)₂ dissolved in 10 ml of anhydrous methanol was dropped under stirring to 0.166 g (0.64 mmol) of 3-(2-fluorophenyl)-1-(4-nitrophenyl)triazene previously dissolved in 30 ml of anhydrous tetrahydrofuran. After 2 h stirring an orange precipitate was isolated and dried in vacuum. The solid was dissolved in 10 ml of pure pyridine. Prismatic orange crystals suitable for X-ray analysis of the title complex are obtained by slow evaporation of the solvent within two weeks.

Properties: orange crystalline substance. C₂₉H₂₁F₂HgN₉O₄ (monomer, 798.14); Yield: 71.5 mg (0.09 mmol), 28% based on Hg(SCN)₂, m.p.: 252–254 °C (decomposition). C, H, N-analysis: Anal. Calc.: C, 43.6; H, 2.7; N, 15.8. Found: C, 43.87; H, 2.87; N, 16.15%.

IR (KBr) *free ligand* 3-(2-fluorophenyl)-1-(4-nitrophenyl)triazene: 3296 (vs, ν (N–H)), 1512 (vs, ν_{as} (NO₂)), 1416 (m, ν (N=N)), 1328 (vs, ν_s (NO₂)), 1256 (vs, ν (F–C_{ar})), 1165 cm⁻¹ (s, ν_s (N–N)).

{Hg^{II}[NNN(PhR)₂]₂Py}₂: the N–H band is absent. 1512 (vs, ν_{as} (NO₂)), 1320 (vs, ν_s (NO₂)), 1268 (s, ν (F–C_{ar})), 1268 cm⁻¹ (s, ν_{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 a Nonius KappaCCD area-detector diffractometer [15]. Cell refinement and the data reduction were performed with *HKL SCALEPACK* and *HKL DENZO*, and *SCALEPACK* [16], respectively. The structure of [Hg^{II}(RPhNNNPhR')₂Py] (R = NO₂, R' = F) was solved by direct methods (SHELXS-97) [17]. Refinements were carried out with the SHELXL-97 [18] 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 analytical method [19].

3. Results and discussion

In the X-ray studies of [Hg^{II}(RPhNNNPhR')₂Py] (R = NO₂, R' = F), the space group *P* $\bar{1}$ reveals to be the correct for the structure solution. Crystal data and experimental conditions of the title complex are given in Table 1. Selected bond distances and angles are listed in Table 2 and Fig. 1 shows the molecular structure of the complex [Hg^{II}(RPhNNNPhR')₂Py] (R = NO₂, R' = F) in a thermal ellipsoid representation [20]. The Hg(II) is quasi-planar coordinated – in an opposite way – by two triazenide ions through two primary Hg–N bonds [Hg–N(11) = 2.093(3), Hg–N(21) = 2.102(3) Å] and two secondary ones

Table 1

Crystal data and structure refinement for $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]_2$

Empirical formula	$\text{C}_{29}\text{H}_{21}\text{F}_2\text{HgN}_9\text{O}_4$
Formula weight	798.14
T (K)	293(2)
Radiation, λ (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	8.83610(10)
b (Å)	12.44830(10)
c (Å)	14.6109(2)
α (°)	65.3260(10)
β (°)	79.6420(10)
γ (°)	79.6490(10)
Volume (Å ³)	1426.71(3)
Z , calculated density (g cm ⁻³)	2, 1.858
Absorption coefficient (mm ⁻¹)	5.461
$F(000)$	776
Crystal size (mm)	0.15 × 0.05 × 0.04 mm
Theta range (°)	2.66–25.09
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-17 \leq l \leq 17$
Reflections collected	22957
Independent reflections (R_{int})	5059 (0.0737)
Completeness to theta max.	99.4%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5059/0/407
Goodness-of-fit on F^2	1.085
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0273$, $wR_2 = 0.0621$
R indices (all data)	$R_1 = 0.0372$, $wR_2 = 0.0652$
Extinction coefficient	0.0045(4)
Largest difference in peak and hole (e Å ⁻³)	0.477 and -0.846

Table 2

Selected bond lengths (Å) and angles (°) for $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]_2$

Bond lengths		Bond angles	
		N(11)–Hg–N(21)	167.40(13)
		N(11)–Hg–N(51)	105.02(12)
		N(21)–Hg–N(51)	87.58(12)
C(22)–F(01)	1.349(5)	N(11)–Hg···N(13)	50.90(11)
C(42)–F(02)	1.355(5)	N(21)–Hg···N(13)	131.89(12)
H(12)···F(02)	2.454	N(51)–Hg···N(13)	85.98(12)
H(32)···F(01)	2.470	N(11)–Hg···N(23)	124.67(11)
H(53)···O(11) ⁱⁱ	2.534	N(21)–Hg···N(23)	49.89(12)
Hg–N(11)	2.093(3)	N(51)–Hg···N(23)	104.44(12)
Hg–N(21)	2.102(3)	N(13)···Hg···N(23)	169.58(10)
Hg–N(51)	2.557(4)	C(35) ⁱ ···Hg···C(34) ⁱ	22.5(1)
Hg···N(13)	2.711(3)	N(12)–N(11)–Hg	113.5(2)
Hg···N(23)	2.780(3)	N(12)–N(13)···Hg	84.6(2)
Hg···C(35) ⁱ	3.461(5)	N(22)–N(21)–Hg	115.0(2)
Hg···C(34) ⁱ	3.570(4)	N(22)–N(23)···Hg	83.5(2)
N(11)–N(12)	1.319(5)	C(12)–H(12)···F(02)	132.47
N(12)–N(13)	1.276(5)	C(32)–H(32)···F(01)	138.11
N(21)–N(22)	1.328(5)	C(53)–H(53)···O(11) ⁱⁱ	132.49
N(22)–N(23)	1.270(5)		

Symmetry transformations used to generate equivalent atoms: (i) $-x + 1, -y, -z$; (ii) $1 + x, -1 + y, z$.

[Hg···N(13) = 2.711(3), Hg···N(23) = 2.780(3) Å]. The square pyramidal configuration of $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]$ is achieved with a neutral pyridine ligand in the apical position [Hg–N(51) = 2.557(4) Å]. The Hg(II) ion is 0.227(2) Å out of the plane settled by the four coordinating nitrogen atoms. The pyridine ring attains with this plane an

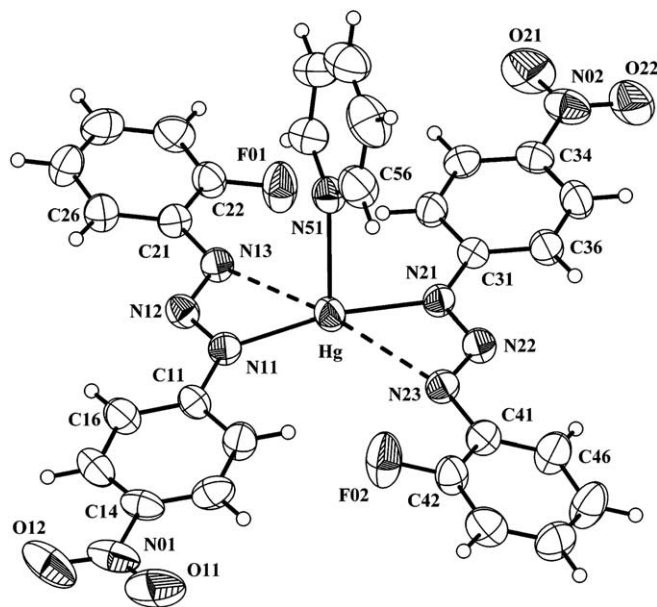


Fig. 1. The molecular structure with atom-labeling scheme of monomer $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]$ ($\text{R} = \text{NO}_2$, $\text{R}' = \text{F}$) [20]. Displacement ellipsoids at the 50% level. Hydrogen atoms are drawn as spheres with an arbitrary radius. Dashed lines represent secondary interactions.

angle of 68.6(1)°. This appreciable deviation of the ideal interplanar angle (90°) can be justified through the non-classical C–H···O hydrogen bonding of the lattice, involving the *meta* C–H group of the pyridine ring. The monomeric $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]$ moieties are linked to pairs as centrosymmetric dimers through reciprocal Hg–arene secondary interactions. Fig. 2 shows a sequence of dimers $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]_2$ ($\text{R} = \text{NO}_2$, $\text{R}' = \text{F}$) linked through the C–H···O secondary bonds along the a axis. 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 C31–C36 ring have remarkably short distances to the Hg(II) ion: these shorter secondary interactions are of 3.461(5) [Hg···C35ⁱ] and 3.570(4) Å [Hg···C34ⁱ], symmetry code (i) $-x + 1, -y, -z$. The distance of the π -interaction from Hg to the midpoint of the C34ⁱ–C35ⁱ bond is 3.51 Å, somewhat larger than the distances from the metallic ion to the midpoint of the C(31ⁱ)–C(36ⁱ) [3.38 Å, symmetry code (i) $x, y - 1, z$] and C25ⁱ–C26ⁱ [3.24(3) Å, symmetry code (i) $1 - x, 1 - y, -z$] bonds in the complexes $\{\text{Hg}[\text{PhN}_3\text{C}_6\text{H}_4\text{N}_3(\text{H})\text{Ph}](\text{NO}_3)\}$ [13] and $\{\text{Hg}[\text{NNN}(\text{PhR})_2]_2\}_n$ ($\text{R} = \text{NO}_2, \text{F}$) [14], respectively. The angles C–Hg–C of the metal–arene π interactions are 22.5(1)° (C34ⁱ···Hg···C35ⁱ), 74.3(3)° (Hg···C34ⁱ–C35ⁱ) and 83.3(3)° (C34ⁱ)–C35ⁱ···Hg, fairly close to the angles found in $\{\text{Hg}[\text{PhN}_3\text{C}_6\text{H}_4\text{N}_3(\text{H})\text{Ph}](\text{NO}_3)\}$ [13] [C31ⁱ···Hg···C36ⁱ = 23(3)°, Hg···C31ⁱ–C36ⁱ = 79(8)°, C31ⁱ–C36ⁱ···Hg = 78(7)°] and $\{\text{Hg}[\text{NNN}(\text{PhR})_2]_2\}_n$ ($\text{R} = \text{NO}_2, \text{F}$) [14] [C25ⁱ···Hg···C26ⁱ = 24.6(1)°, Hg···C25ⁱ)–C26ⁱ = 84.4(3), C25ⁱ)–C26ⁱ···Hg = 71.0(3)].

The dimeric moieties $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]_2$ attain additionally intramolecular, secondary C–H···F interac-

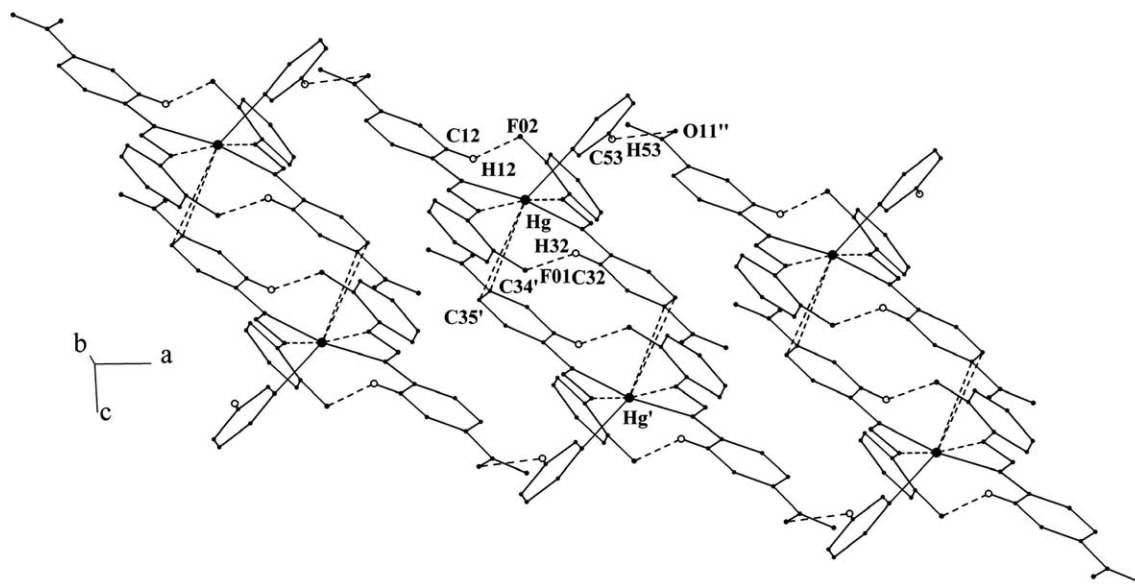


Fig. 2. Section of the unidimensional supramolecular array of $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]_2$ complexes. Shown are three dimers linked by $\text{Hg}-\eta^2$ -arene π -interactions and the $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds which link these dimers to a chain propagating along the a axis. Dashed lines represent secondary interactions. Symmetry transformations used to generate equivalent atoms: (') $-x+1, -y, -z$; (") $1+x, -1+y, z$.

tions with asymmetrical distances and angles (see Fig. 2): $\text{C}12\cdots\text{F}02 = 3.158(6) \text{ \AA}$; $\text{C}12-\text{H}12\cdots\text{F}02 = 132.47^\circ$, $\text{C}32\cdots\text{F}01 = 3.223(5) \text{ \AA}$; $\text{C}32-\text{H}32\cdots\text{F}01 = 138.11^\circ$. The dimeric units are assembled by translation in the crystallographic direction $[100]$ to unidimensional chains linked through the already mentioned non-classical $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds ($\text{C}53\cdots\text{O}11'' = 3.236(6) \text{ \AA}$; $\text{C}53-\text{H}53\cdots\text{O}11'' = 132.49^\circ$, symmetry code (") $1+x, -1+y, z$). In the unit cell these chains are related in pairs through an inversion centre, without (extended) bidimensional interactions.

As a conclusion, the monomeric complexes $[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]$ represented in Fig. 1 can be viewed as *tectonic units* [21] which assemble the whole lattice of "polymeric" $\{[\text{Hg}^{\text{II}}(\text{RPhNNNPhR}')_2\text{Py}]_2\}_n$ through intermolecular metal-arene π interactions and $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding. Blocking one of the axial coordination positions of the $\text{Hg}(\text{II})$ ion with pyridine opened the possibility to achieve a $\text{Hg}-\eta$ -arene dimerization.

4. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre CCDC No. 286424. 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).

References

- [1] I. Haiduc, J. Zukerman-Schpector, Phosphorus, Sulfur Silicon 171 (2001) 171.
- [2] J. Zukerman-Schpector, I. Haiduc, Cryst. Eng. Commun. 4 (2002) 178.
- [3] J. Bergman, J. Siden, K. Maraartmann-Moe, Tetrahedron 40 (1984) 1607.
- [4] R.K. Chadha, J.E. Drake, M.A. Khan, Can. J. Chem. 62 (1984) 32.
- [5] F. Einstein, J. Trotter, C.S. Williston, J. Chem. Soc. A (1967) 2018.
- [6] B. Krebs, V. Paulat, Eur. Cryst. Meet. (1974) 238.
- [7] B. Krebs, F.-P. Ahlers, Adv. Inorg. Chem. 35 (1990) 235.
- [8] A.K.S. Chauhan, Anamika, A. Kumar, R.C. Srivastava, R.J. Butcher, J. Beckmann, A. Duthie, J. Organomet. Chem. 690 (2005) 1350.
- [9] G. Llabres, O. Dieberg, L. Dupont, Acta Crystallogr. Sect. B 28 (1972) 2438.
- [10] M.R. Detty, J.M. McKelvey, H.R. Luss, Organometallics 7 (1988) 1131.
- [11] J. Zukerman-Schpector, J.V. Comasseto, H.A. Stefani, Acta Crystallogr. Sect. C 51 (1995) 861.
- [12] J. Zukerman-Schpector, E.E. Castellano, G. Oliva, J.V. Comasseto, H.A. Stefani, Acta Crystallogr. Sect. C 47 (1991) 960.
- [13] M. Hörner, A.J. Bortoluzzi, J. Beck, M. Serafin, Z. Anorg. Allg. Chem. 628 (2002) 1104.
- [14] M. Hörner, G. Manzoni de Oliveira, J.S. Bonini, H. Fenner, Supramolecular assemblages through metal- η^4 -arene π -interactions: Synthesis and X-ray characterization of $\{\text{Hg}^{\text{II}}[\text{NNN}(\text{PhR})_2]_2\}_n$ ($\text{R} = \text{NO}_2, \text{F}$), a bis diaryl-substituted triazenide complex polymer of $\text{Hg}(\text{II})$, J. Organomet. Chem., in press.
- [15] Nonius COLLECT, Nonius BV, Delft, The Netherlands, 1997–2000.
- [16] Z. Otwinowski, W. Minor, in: C.W. Carter Jr., R.M. Sweet (Eds.), Methods in Enzymology, Macromolecular Crystallography, Part A, vol. 276, Academic Press, New York, 1997, p. 307.
- [17] G.M. Sheldrick, SHELXS-97, Program for Crystal Structure Solution, University of Göttingen, Germany, 1997.
- [18] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [19] N.W. Alcock, in: F.R. Ahmed, S.R. Hall, P. Huber (Eds.), Crystallographic Computing, Munksgaard, Copenhagen, 1970, p. 271.
- [20] K. Brandenburg. DIAMOND. 1996, Version 1.1a., Crystal Impact GbR, Bonn, Germany.
- [21] P.D. Boyle, S.M. Godfrey, Coord. Chem. Rev. 223 (2001) 265.