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TTF and TCNQ adducts of trimeric perfluoro-*ortho*-phenylene mercury

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Abstract

Combinaison de trimère de perfluoro-*ortho*-phénylène mercure (**1**) avec le TTF et le TCNQ dans un mélange 1:1 de CH₂Cl₂ et de CS₂ suivie de l'évaporation lente du solvant mène à la cristallisation de [(**1**)₂·TTF] (**2**), qui est isolé sous forme d'aiguilles oranges. La même expérience, faite en remplaçant le TTF par le TCNQ, mène à la formation de cristaux jaunes de [(**1**)₂·TCNQ] (**3**). La structure des deux composés a été déterminée par diffraction des rayons X. La structure du composé **2** à l'état solide se compose de supramolécules centrosymétriques de [(**1**)₂·TTF]. Dans ces supramolécules, la molécule de TTF est prise en sandwich entre deux molécules de **1**. Des interactions secondaires entre les atomes de soufre et les atomes de mercure, comprises entre 3.467(5) Å et 3.533(5) Å, assurent la cohésion de cette supramolécule. Dans le cas de **3**, la structure du composé à l'état solide se compose aussi de supramolécules centrosymétriques de [(**1**)₂·TCNQ]. Dans ce cas-là, cependant, la molécule de TCNQ est presque perpendiculaire aux molécules de **1** avoisinantes, avec lesquelles elle interagit par coordination de deux des groupements nitriles aux atomes de mercure. Un examen de la structure indique que l'atome d'azote de la fonction nitrile interagit de manière simultanée avec les trois atomes de mercure du composé **1**. Les longueurs des interactions entre les atomes de mercure et l'atome d'azote sont comprises entre 3.102(11) et 3.134(11) Å. **To cite this article:** M.R. Haneline et al., *C. R. Chimie* 7 (2004).

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Résumé

La combinaison du trimère du perfluoro-*ortho*-phénylène mercure (**1**) avec le TTF dans un mélange 1:1 de CH₂Cl₂ et de CS₂ suivie par l'évaporation lente du solvant mène à la cristallisation de [(**1**)₂·TTF] (**2**), qui est isolé sous forme d'aiguilles oranges. La même expérience, faite en remplaçant le TTF par le TCNQ, mène à la formation de cristaux jaunes de [(**1**)₂·TCNQ] (**3**). La structure des deux composés a été déterminée par diffraction des rayons X. La structure du composé **2** à l'état solide se compose de supramolécules centrosymétriques de [(**1**)₂·TTF]. Dans ces supramolécules, la molécule de TTF est prise en sandwich entre deux molécules de **1**. Des interactions secondaires entre les atomes de soufre et les atomes de mercure, comprises entre 3.467(5) Å et 3.533(5) Å, assurent la cohésion de cette supramolécule. Dans le cas de **3**, la structure du composé à l'état solide se compose aussi de supramolécules centrosymétriques de [(**1**)₂·TCNQ]. Dans ce cas-là, cependant, la molécule de TCNQ est presque perpendiculaire aux molécules de **1** avoisinantes, avec lesquelles elle interagit par coordination de deux des groupements nitriles aux atomes de mercure. Un examen de la structure indique que l'atome d'azote de la fonction nitrile interagit de manière simultanée avec les trois atomes de mercure du composé **1**. Les longueurs des interactions entre les atomes de mercure et l'atome d'azote sont comprises entre 3.102(11) et 3.134(11) Å. **Pour citer cet article :** M.R. Haneline et al., *C. R. Chimie* 7 (2004). © 2004 Académie des sciences. Published by Elsevier SAS. All rights reserved.

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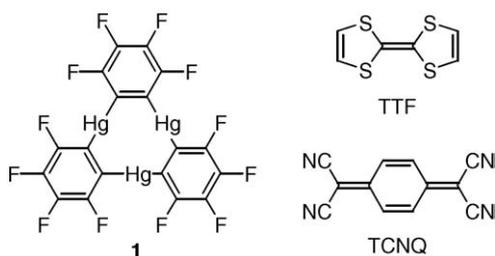
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Keywords: Lewis acids; Mercury; TTF; TCNQ; π -interactions; Supramolecular chemistry

Mots-clés : Acides de Lewis ; Mercure ; TTF ; TCNQ ; Interactions π ; Chimie supramoléculaire

1. Introduction

Trimeric perfluoro-*ortho*-phenylene mercury (**1**) [1] is a simple trifunctional Lewis acid that has been used for the complexation of both anionic and neutral Lewis basic substrates [2–7]. In a series of studies, we also demonstrated that this trinuclear mercury derivative readily complexes with aromatic substrates including benzene, naphthalene, biphenyl, pyrene and triphenylene [8–11]. The resulting adducts consists of supramolecular stacks in which the arene interacts with the mercury centers of **1** through secondary mercury- π interactions. It occurred to us that similar structures might result from the interaction of **1** with more π -basic molecules. As a result, we have investigated its interaction with tetrathiafulvalene (TTF). As part of this work and in order to shed further light on the chemical affinity of **1**, we have also studied its interaction with the typical π -acidic 7,7,8,8-tetracyanoquinodimethane (TCNQ). These efforts were further motivated by a series of recent investigations in which it has been demonstrated π -basic trinuclear gold(I) derivatives interact with various π -acidic molecules including C_6F_6 , TCNQ [12] and nitrofluorenones [13].



2. Results and discussion

When **1** and TTF are combined in a 1:1 mixture of CH_2Cl_2 and CS_2 , slow evaporation of the solvent leads to the formation of orange needles of the 2:1 adduct $[(1)_2 \cdot TTF]$ (**2**). Interestingly, a similar experiment carried out with TCNQ affords light yellow needles of an adduct of identical stoichiometry, namely

$[(1)_2 \cdot TCNQ]$ (**3**). In both cases, the color of these complexes corresponds to that of the organic molecule which rules out the presence of intense charge transfer bands. The ^{199}Hg , ^{19}F , and 1H NMR spectra of these compounds in CD_2Cl_2 as well as their UV absorption spectra correspond to those of the free molecular components which indicates complete dissociation of the adducts upon dissolution.

Compound **2** crystallizes in the triclinic space group $P\bar{1}$ with one centrosymmetrical $[(1)_2 \cdot TTF]$ adduct per unit cell (Table 1, Fig. 1). Examination of the structure indicates that each molecule of TTF is sandwiched by two molecules of **1** and engages in multiple Hg...S secondary interactions. Taking into account the range of values that have been suggested for the van der Waals radii of both mercury ($r_{vdw} = 1.73$ – 2.00 Å) [14,15] and sulfur ($r_{vdw} = 1.8$ – 2.03 Å) [16–19], the length of these interactions appears to be either close to or shorter than the sum of the van der Waals radii of the two elements and mercury. As shown in Fig. 1, the S(1) and S(2) atoms coordinate to the Hg(3) mercury center in a bidentate fashion (Hg(3)–S(1) 3.467(5) Å, Hg(3)–S(2) 3.533(5) Å). The sulfur atom S(1) forms an additional interaction with the mercury center Hg(2) (Hg(2)–S(1A) 3.529(5) Å). These secondary interactions are comparable to those found in $[1 \cdot SCN]^-$ [2] and $[1 \cdot \mu_6-SMe_2]_n$ [20]. They are also respectively longer and shorter than the primary Hg–S bond (2.40 Å) and the secondary Hg...S interactions (3.89 Å) observed in the structure of $[tth \cdot HgCl_2]$. The structure of $[tth \cdot HgCl_2]$ features short intramolecular primary Hg–S bonds and long intermolecular secondary Hg–S interactions [21]. It is interesting to point to the structural resemblance that exists between **2** and a series of gold-containing supramolecules reported by Balch [13] as well as Burini and Fackler [22]. As mentioned earlier, these supramolecules consist of stacks in which trinuclear gold(I) complexes alternate with organic derivatives such as fluorenones, hexafluorobenzene, and TCNQ [12]. At the difference of **2**, the trinuclear gold(I) complexes are electron-rich while the organic substrates are electron-poor. Compound **2**, which contains electron-poor mercury centers and electron-rich

Table 1
Crystal data, data collection, and structure refinement for **2** and **3**-(CS₂)₃

Crystal data	2	3 -(CS ₂) ₃
Formula	C ₄₂ H ₄ F ₂₄ Hg ₆ S ₄	C ₅₁ H ₄ F ₂₄ Hg ₆ N ₄ S ₆
<i>M_r</i>	2296.23	2524.48
Crystal size (mm ³)	0.29 × 0.055 × 0.055	0.31 × 0.15 × 0.080
Crystal system	Triclinic	Triclinic
Space group	P $\bar{1}$	P $\bar{1}$
<i>a</i> (Å)	8.9347(18)	8.9533(18)
<i>b</i> (Å)	10.017(2)	12.038(2)
<i>c</i> (Å)	13.669(3)	14.641(3)
α (°)	87.57(3)	96.47(3)
β (°)	75.12(3)	96.35(3)
γ (°)	78.75(3)	109.82(3)
<i>V</i> (Å ³)	1159.5(4)	1456.3(5)
<i>Z</i>	1	1
ρ_{calc} (g cm ⁻³)	3.288	2.878
μ (Mo <i>K</i> α) (mm ⁻¹)	20.098	16.088
<i>F</i> (000) (e)	1016	1130
Data collection		
<i>T</i> (K)	293(2)	293(2)
Scan mode	ω	ω
<i>hkl</i> range	-10→9, -11→11, -16→16	-10→10, -14→14, -17→16
Measured refl.	11 377	13 915
Unique refl., [<i>R</i> _{int}]	4068 [0.0486]	5088 [0.0286]
Refl. used for refinement	4068	5088
Absorption correction	SADABS	SADABS
<i>T</i> _{min} / <i>T</i> _{max}	0.122867	0.315385
Refinement		
Refined parameters	343	412
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ(<i>I</i>)]	0.0443, 0.1168	0.0460, 0.1091
ρ_{fin} (max/min) (e Å ⁻³)	2.319, -1.982	4.332, -1.558
^a <i>R</i> 1 = (F _o - F _c)/F _o ; ^b <i>wR</i> 2 = { [w(F _o ² - F _c ²)]/[w(F _o ²)] } ^{1/2} ; w = 1/[σ ² (F _o ²) + (ap) ² + bp]; p = (F _o ² + 2 F _c ²)/3; a = 0.0851 (2), 0.0808 (3); b = 0 (2), 15.0890 (3).		

TTF molecules, can therefore be regarded as the charge-reverse analogue of the gold assemblies.

As in the case of **2**, compound **3** crystallizes in the triclinic P $\bar{1}$ space group with one centrosymmetrical [(**1**)₂·TCNQ] adduct per unit cell that also contains three molecules of CS₂ (Table 1, Figs. 2–4). Examination of the atomic connectivity reveals the simultaneous coordination of one of the nitrile nitrogen atoms to the three mercury centers of **1** (Fig. 1). The resulting

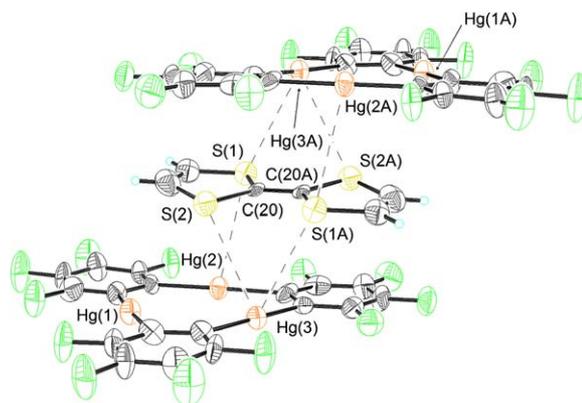


Fig. 1. Crystal structure of **2**. Mercury (orange), sulfur (yellow), fluorine (green), and carbon (black). Intramolecular distances (Å): Hg(2)–S(1) 3.529(5), Hg(3)–S(2) 3.533(5), Hg(3)–S(1A) 3.467(5). Intermolecular bond distances (Å) and angles (°): Hg(1)–C(8) 2.111(14), Hg(1)–C(1) 2.122(14), Hg(2)–C(7) 2.051(13), Hg(2)–C(14) 2.086(15), Hg(3)–C(2) 2.041(16), Hg(3)–C(13) 2.069(15), C(20)–C(20A) 1.37(2), S(1)–C(20) 1.779(13), S(2)–C(20) 1.729(13), C(8)–Hg(1)–C(1) 174.8(6), C(7)–Hg(2)–C(14) 176.4(7), C(2)–Hg(3)–C(13) 174.4(6), S(2)–C(20)–S(1) 114.4(7).

Hg–N distances range from 3.102(11) to 3.134(11) Å and are well within the sum of the van der Waals radii for mercury ($r_{\text{vdw}} = 1.73\text{--}2.00$ Å) [14,15] and nitrogen ($r_{\text{vdw}} = 1.60$ Å). As a result of these interactions, the nitrogen atom (N(1)) is essentially equidistant from the three Lewis acidic sites and sits at 2.32 Å from the plane defined by the three mercury atoms. The linear nitrile functionality is almost perpendicular to the plane of the trinuclear complex with which it forms an angle of 88.7°. The metrical and angular parameters observed in **3** resemble those encountered in the acetonitrile adduct [**1**·(μ_3 -acetonitrile)₂] [23,24] (avg. Hg–N = 2.96 Å). Adducts involving acetonitrile and mercuracarborands have also been isolated [25]. The *trans* nitrile group of the TCNQ molecules coordinates to another molecule of **1** thus completing the [(**1**)₂·TCNQ] unit. The remaining two nitrile groups of the TCNQ molecule do not engage in any donor interactions. Three molecules of CS₂ are trapped between neighboring [(**1**)₂·TCNQ] units and interact with the mercury centers of the juxtaposed molecules of **1** (Fig. 3). Two of these molecules are symmetrically equivalent and are terminally ligated to the mercury center Hg(2) (Hg(2)–S(2) 3.532(6) Å). The third molecule of CS₂ is centrosymmetrical and interacts via each of its two sulfur atoms with four mercury centers provided by the two molecules of **1** (Hg(2)–S(3)

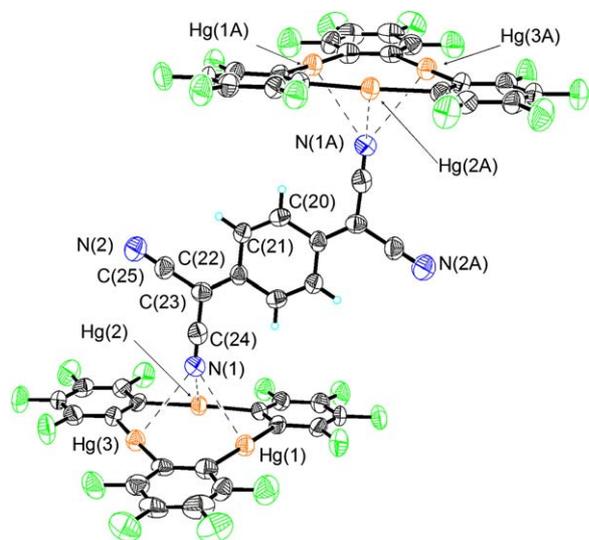


Fig. 2. Crystal structure of **3** illustrating the Hg–N interactions. Mercury (orange), fluorine (green), nitrogen (blue), carbon (black). Intramolecular distances (Å): Hg(1)–N(1) 3.102(11), Hg(2)–N(1) 3.128(12), Hg(3)–N(1) 3.134(11). Intermolecular bond distances (Å) and angles (°): Hg(1)–C(1) 2.089(14), Hg(1)–C(8) 2.099(12), Hg(2)–C(14) 2.104(12), Hg(2)–C(7) 2.109(12), Hg(3)–C(13) 2.079(14), Hg(3)–C(2) 2.079(13), N(1)–C(24) 1.157(17), N(2)–C(25) 1.130(18), C(20)–C(21) 1.335(18), C(21)–C(22) 1.438(17), C(22)–C(23) 1.366(17), C(23)–C(24) 1.424(18), C(23)–C(25) 1.449(18), C(1)–Hg(1)–C(8) 175.3(5), C(14)–Hg(2)–C(7) 176.0(5), C(13)–Hg(3)–C(2) 176.2(5), C(24)–C(23)–C(25) 116.1(11), N(1)–C(24)–C(23) 178.6(15), N(2)–C(25)–C(23) 177.8(17).

3.640(7) Å, Hg(3)–S(3) 3.485(6) Å). These Hg...S distances are comparable to those observed in the structure of **2** and are once again comparable or shorter than the sum of the van der Waals radii of the two elements. As a result of these interaction, the solid-state structure of **3**–(CS₂)₃ consists of extended one-dimensional chain, as depicted in Fig. 4.

3. Conclusions

The results reported herein further document the acceptor ability of **1**. While known π -donors such as TTF coordinate to **1** in a stacking fashion, known π -acceptors such as TCNQ interact with **1** through the electron rich terminus of the nitrile groups. These results clearly indicate that compound **1** is a Lewis acid. It is also important to note that the spectroscopic and structural results presented herein do not support oxidation of the TTF molecules. As a result, compound **2**

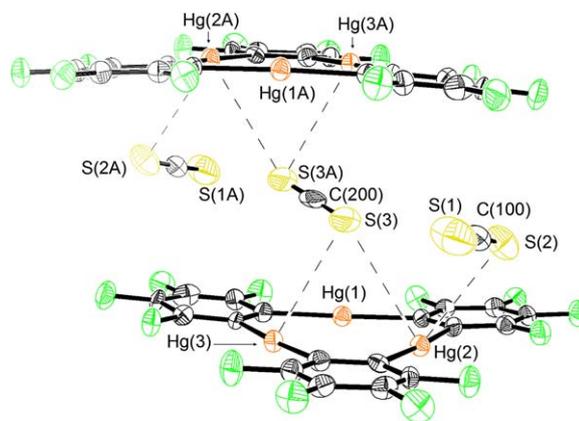


Fig. 3. Crystal structure of **3** illustrating the Hg–S interactions. Mercury (orange), fluorine (green), sulfur (yellow), carbon (gray). Intramolecular distances (Å): Hg(2)–S(2) 3.532(6), Hg(2)–S(3) 3.640(7), Hg(3)–S(3) 3.485(6). Intermolecular bond distances (Å) and angles (°): S(1)–C(100) 1.57(3), S(2)–C(100) 1.51(2), S(3)–C(200) 1.553(11), S(2)–C(100)–S(1) 174.6(18), S(3)–C(200)–S(3A) 180.0(16).

cannot be described as a charge transfer salt. Rather, its cohesion apparently results from the presence of secondary donor interaction occurring between the sulfur atoms of TTF and the mercury centers of **1**.

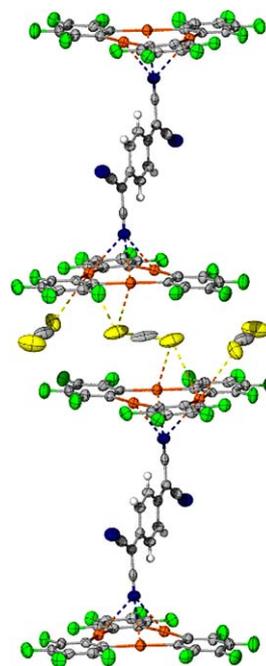


Fig. 4. Extended structure of **3**. Mercury (orange), fluorine (green), nitrogen (blue), sulfur (yellow), carbon (gray).

4. Experimental

4.1. Materials and methods

Due to the toxicity of the mercury compounds discussed in these studies, extra care was taken at all times to avoid contact with solid, solution, and airborne particulate mercury compounds. The studies herein were carried out in well-aerated fume hood. The infrared spectra were recorded as KBr pellets on a Mattson Genesis Series FTIR. Atlantic Microlab, Inc., Norcross, GA, performed the elemental analyses. TTF was purchased from TCI America and used as provided. Other commercially available starting materials and solvents were purchased from Aldrich Chemical and were used as provided. Compound **1** was prepared according to the published procedure outlined by Sartori and Golloch [1].

4.2. Synthesis of $I_2\cdot TTF$ (**2**)

Compound **1** (100 mg, 9.6 μmol) was dissolved in a 1:1 mixture of CS_2 and CH_2Cl_2 (30 ml). In a separate vial TTF (10 mg, 5.1 μmol) was dissolved in a 1:1 mixture of CS_2 and CH_2Cl_2 (3 ml). The two solutions were mixed thoroughly. Partial evaporation of the solvent resulted in the crystallization of **2**, which was isolated in a 70% yield (153 mg, 6.7 μmol). mp decomposition 285 °C. Anal. calc. (found) for $\text{C}_{42}\text{H}_4\text{F}_{24}\text{Hg}_6\text{S}_4$: C, 21.96 (22.16); H, 0.18 (0.16).

4.3. Synthesis of $I_2\cdot\text{TCNQ}\cdot 3\text{CS}_2$ (**3**–(CS_2)₃)

Compound **1** (100 mg, 9.6 μmol) was dissolved in a 1:1 mixture of CS_2 and CH_2Cl_2 (30 ml). In a separate vial, TCNQ (10 mg, 5.2 μmol) was dissolved in a 1:1 mixture of CS_2 and CH_2Cl_2 (3 ml). The two solutions were mixed thoroughly. Partial evaporation of the solvent resulted in the crystallization of **3**, which was isolated in a 22.7% yield (30 mg, 1.2 μmol), mp decomposition 275 °C. Anal. calc. (found) for $\text{C}_{51}\text{H}_4\text{F}_{24}\text{Hg}_6\text{N}_4\text{S}_6$: C, 24.26 (23.78); H, 0.16 (0.15).

4.4. Crystal structures

X-ray data for **2** and **3** were collected on a Bruker SMART-CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Speci-

mens of suitable size and quality were selected and glued onto a glass fiber with superglue. The structure was solved by direct methods, which successfully located most of the non-hydrogen atoms. Subsequent refinement on F^2 using the SHELXTL/PC package (version 5.1) allowed location of the remaining non-hydrogen atoms. Further crystallographic details can be found in Table 1 and in the Supporting Information.

Acknowledgments

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Supplementary material

Crystallographic data, atomic coordinates for compounds **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK as deposition number CCDC 224188 & 224189, and can be obtained by contacting the CCDC.

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