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Synthesis and structural characterization of a binary metal cluster and a coordination polymer based on the mercury Bis(phenylselenolate) unit

Ana B. Lago [a,*], Ernesto S. Lang [b], Bárbara Tirloni [b], Ezequiel M. Vázquez-López [a]

[a] *Departamento de Química Inorgánica, Facultade de Química, Universidade de Vigo, E-36310 Vigo, Galicia, Spain*
[b] *Departamento de Química, Laboratório de Materiais Inorgânicos, Universidade Federal de Santa Maria, 97.105-900 Santa Maria, RS, Brazil*

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ABSTRACT

The versatile coordination chemistry of the Bis(phenylselenolate) ($Hg(SePh)_2$) with $Hg(SCN)_2$ salt allows the synthesis of a cluster and a 2D coordination polymer. The reaction at low temperature in dimethylformamide (dmf) affords single crystals containing neutral clusters with the formula $[Hg_8S(SCN)_2(SePh)_{12}(dmf)_2]$ (**1**). Then, the 2D coordination polymer [Hg(SCN)(SePh)] (**2**) is obtained in comparable yielding. The use of bis(2-pyridylthio)methane as secondary ligand significantly improves the synthesis of **2**, since it is synthesized at room temperature, in a short time and in a good yield. The effects of the weak interactions in the crystal packing were also analyzed.

1. Introduction

Metal chalcogenolate complexes have attracted interest due to their rich structural chemistry, as well as other materials and biological applications such as precursor for M/Se materials or model for active sites of chacolgen-containing metalloproteins [1].

The construction of new organochalcogenide compounds using $Hg(EPh)_2$ (E = Se, Te) units and suitable metal salts have shown to be an efficient way to generate new organochalcogenide compounds in form of clusters or polymeric structures [2].

In previous works we have investigated the reaction of $Hg(EPh)_2$ with halide mercury salts HgX_2 yielding clusters with the general formula $[Hg_3X_3(EPh)_3]$.2dmso [3] and other larger clusters as $[Hg_6(\mu\text{-}Br_2)Br_2(\mu\text{-}TePh)_8(py)_2]$ [4] and $[Hg_8(\mu\text{-}n\text{-}C_3H_7Te)_{12}(\mu\text{-}Br)Br_3]$ [5].

We have also studied the opening of the six-membered ring Hg_3Te_3 of $[Hg_3Cl_3(\mu\text{-}TePh)_3]\cdot 2dmso$ by redissolution with dmso, reacting with $Co[Hg(SCN)_4]$ to afford the polymeric compound $[(dmso)_2Co(NCS)_4(Hg\text{-}TePh)_2]_n$ [6].

Nevertheless, the use of the pseudohalide $Hg(SCN)_2$ as mercury salt precursor give rise to new neutral cluster or polymeric compounds, shown the great versatility of the thiocyanate anion as ligand. The SCN^- anion exhibit several remarkable peculiarities that is (i) variety of bonding modes (terminal or bridging), (ii) it can act as N-bonded or S-bonded to the metal and, (iii) it can act as acceptor or donor in different weak interactions [7].

On the other hand, the synthesis of chemical compounds at room temperature and atmospheric pressure are possible if these compounds are thermodynamically and (or) kinetically stable in these conditions. Nevertheless the synthesis of coordination polymers and cluster compounds has significant difference features. For cluster compounds the essential problems are the stability of the cluster ion itself, the appropriate ligands selection required and the small-scale quantity of compound obtained in synthesis [8].

The synthesis of metal coordination polymers has attracted significant interest as they represented an important interface between synthetic chemistry and material science. In contrast to coordination polymers of transition metal ions, the formation of polymers with heavy metal ions such as mercury(II) seems to be surprisingly sparse [9]. In addition, multidimensional coordination polymers consisting of oligonuclear metal clusters can be potential candidates for various applications including gas storage and catalysis [10].

In previous studies, bis(2-pyridylthio)methane (2bpytm) (Scheme 1) have been extensively used to prepare metal–organic frameworks with different metal centers allowing the isolation of different structural motifs [11]. Furthermore, cleavage and partial oxidation of 2bpytm have led to the isolation of diverse compounds resulting from C–S bond scission [12]. So that, to date the organic molecule 2bpytm has shown to be a multifunctional compound.

2. Experimental

2.1. Materials and physical measurements

Elemental analyses (C, H, N, S) were carried out with a Fisons EA-1108 microanalyser. Melting points (m.p.) were measured with a Gallenkamp MBF-595 apparatus. IR spectra were recorded from KBr discs (4000–400 cm^{-1}) with a Jasco FT/IR-6100 spectrometer.

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* Corresponding author.
E-mail address: ablago@uvigo.es (A.B. Lago).

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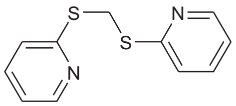

Scheme 1. The molecular structure of the ligand 2bpytm.

TGA was performed on a SETSYS Evolution Setaram thermogravimetric analyzer in flowing N_2 with a heating rate of 10 °C min^{-1}. X-ray powder diffraction (XRPD) characterization was performed using a Siemens D-5000 diffractometer with Cu Kα radiation (λ = 1.5418 Å) over the range 5.0–60.0° in steps of 0.20° (2θ) with a count time per step of 5.0 s.

2.2. Synthesis

2.2.1. [$Hg_8S(SCN)_2(SePh)_{12}(dmf)_2$] (**1**)

A solution of $Hg(PhSe)_2$ [13] (0.102 g, 0.2 mmol) in dmf (10 mL) was added dropwise to a solution of $Hg(SCN)_2$ (0.062 g, 0.2 mmol) in dmf (10 mL). The resulting solution was stirred for 4 h at room temperature. The mother liquor afforded crystals at 4 °C in 15 days that were identified as **1**.

Yield: 0.041 g, 35% based on $Hg(PhSe)_2$. M.p. 130 °C. *Anal.* calc. for $C_{80}H_{74}N_4S_3O_2Se_{12}Hg_8$: C, 25.47; H, 1.98; N, 1.49; S, 2.55. Found: C, 25.65; H, 1.72; N, 1.62; S, 2.73%. IR (KBr, cm^{-1}): 3433, [ν_s(C–H)]; 2109, [ν_s (S=C=N)]; 1638, [ν_s (C=O)]; 1570, 1470, 1434 [ν_s (C=C)]; 1064, 1018, 998 [δ(C=C–H)]; 733,686 cm^{-1} [δ(C=C–H)].

2.2.2. [Hg(SCN)(SePh)] (**2**)

Compound **2** was obtained as a by-product of the synthesis of **1** and also in presence of the secondary ligand bis(2-pyridylthio)methane (2bpytm) [11a].

Method (a): Once single crystals of **1** were filtered off, the mother liquor afforded new crystals after 5 days at 4 °C that were identified as **2**. Yield: 30%.

Method (b): A solution of 2bpytm (0.047 g, 0.2 mmol) in a 1:2 mixture of ethyl acetate and acetonitrile (5 mL) was added dropwise to a solution of $Hg(SCN)_2$ (0.062 g, 0.2 mmol) in the same solvent mixture (5 mL) together with dmf (2 mL). The resulting solution was stirred for 4 h and a solution of $Hg(PhSe)_2$ (0.102 g, 0.2 mmol) in dmf (5 mL) was added dropwise, and stirred for 4 h more. Crystals suitable for X-ray diffraction were obtained from the mother liquor in one day at room temperature.

Table 1
Crystal and structure refinement data.

Compound	1	2
Empirical formula	$C_{80}H_{74}O_2S_3N_4Se_{12}Hg_8$	$C_{14}H_{10}S_2N_2Se_2$Hg2
Formula weight	3771.85	829.46
T (K)	100(2)	293(2)
Crystal system	orthorhombic	monoclinic
Space group	*Pbcn*	*P*21/c
Unit cell dimensions		
a (Å)	13.6141(2)	10.8907(6)
b (Å)	25.7190(5)	10.9479(5)
c (Å)	26.1983(4)	7.3598(3)
A (°)	90	90
β (°)	90	100.771(2)
γ (°)	90	90
V (Å^3)	9173.1(3)	862.03(7)
Z	4	2
ρ_{calc} (g cm^{-3})	2.731	3.196
Absorption coefficient (mm^{-1})	18.211	22.248
F(000)	6776	736
Crystal size (mm)	0.24 × 0.05 × 0.04	0.052 × 0.132 × 0.203

Yield: 60%. M.p. 165 °C. *Anal.* calc. for $C_{14}H_{10}N_2S_2Se_2Hg_2$: C, 20.15; H, 1.21; N, 3.36; S, 7.67. Found: C, 20.28; H, 1.30; N, 3.30; S, 7.35%. IR (KBr, cm^{-1}): 3437, [ν_s(C–H)]; 2096, [ν_s (S=C=N)]; 1570, 1473, 1436 [ν_s (C=C)]; 1063, 1019, 998 [δ(C=C–H)]; 733,6846 cm^{-1} [δ(C=C–H)].

2.3. Crystallography

Crystallographic data of **1** and **2** were collected on a Bruker Kappa Apex II CCD diffractometer at 293 K using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) and were corrected for Lorentz and polarization effects. The frames were integrated with the Bruker SAINT [14] software package and the data were corrected for absorption using the program SADABS [15].

The structures were solved by direct methods using the program SHELXS97 [16]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least-squares calculations on F^2 using the program SHELXL97 [17]. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters. Drawings were produced with MERCURY [18] program and special computations for the crystal structure discussions were carried out with PLATON [19]. Crystal data and structure refinement data are listed in Table 1.

The nature of the central atom of the cluster **1** as sulfur was confirmed by X-ray photoelectron spectroscopy (XPS) on the single crystal and elemental analysis of the solid. However, when selenium is included as the central atom, the thermal parameter is 0.749(7) against 0.0369(4) with sulfur atom. Refinement of the model considering a S/Se disorder at this position were also unsuccessful.

3. Result and discussion

In this paper we describe the synthesis and structural characterization of two kind of compounds: the discrete cluster [$Hg_8S(SCN)_2(SePh)_{12}(dmf)_2$] (**1**) and the 2D coordination polymer [Hg(SCN)(SePh)] (**2**). The organic molecule 2bpytm contributes to the isolation of the coordination polymer **2**.

Both compounds were obtained by mild synthetic strategies from equimolar mixture of the both metal salts, in a relatively short time and were clearly stable under normal atmosphere and at room temperature. The compounds were characterized by elemental analysis, infrared spectroscopy and single-crystal X-ray diffraction. The powder X-ray diffraction experiments were compared with the simulated from the crystals structure showing that the crystal is representative of the bulk materials (Supplementary Information). The surface analysis technique X-ray photoelectron spectroscopy (XPS) show that the atomic relation Hg:Se:S is 1:1:1 in **2** and 2:3:1 in **1**. The %w of Hg:Se:S is according with the values expected (Supplementary Information).

The melting point of the cluster compound is considerably lower than polymeric compound **2**. Thermogravimetric analysis (TGA) of compound **2** shows that the thermal decomposition occurs in two-step process between r.t. and 475 °C. The first weight loss of 46% between 165 °C and 300 °C suggests that both ligands are cleaved in this step (theorethical weight loss of 51%).

The infrared spectra of both compounds show the characteristic absorption bands of the phenyl rings [20]. A broad band with a medium intensity is observed in **1** at 2109 cm^{-1} due to the thiocyanate acting as terminal group. These bands indicate that the thiocyanate group acts as monodentate ligand, most probably through the sulfur atoms [21]. On the other hand, the thiocyanate group that forms a bridge between two mercury atoms in **2**, shows a

$$Hg(PhSe)_2 \quad + \quad HgX_2 \quad \rightarrow \quad 2\ PhSeHgX$$

Scheme 2. The formation of precurssor PhSeHgX.

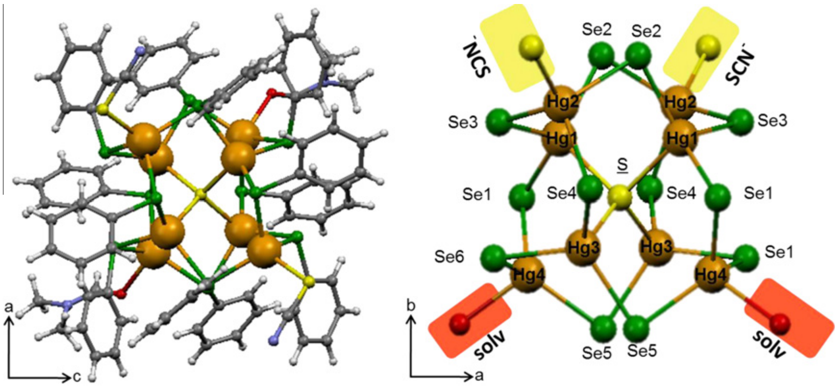

Fig. 1. Structure of cluster **1** (the H atoms are omitted for clarity) and schematic representation showing the position of SCN⁻ ligands and solvent molecules.

Table 2
Selected bond lengths (Å) and angles (°) for **1**.

Distances			
Hg(4)–O(1S)	2.469(7)	Se(6)–Hg(3)	2.6607(9)
S–Hg(1)	2.5571(11)	S–Hg(3)	2.5831(9)
Angles			
C(11)–Se(1)–Hg(4)	106.8(3)	Se(3)–Hg(1–Se(1)	111.82(3)
C(11)–Se(1)–Hg(1)	97.2(3)	S(1)–Hg(2)–Se(3)#1	115.03(7)
Hg(4)–Se(1)–Hg(1)	89.03(3)	S(1)–Hg(2)–Se(2)	103.55(8)
C(21)–Se(2)–Hg(1)	97.4(3)	Se(3)#1–Hg(2)–Se(2)	113.25(3)
C(21)–Se(2)–Hg(2)	105.7(3)	S(1)–Hg(2)–Se(4)	103.27(7)
Hg(1)–Se(2)–Hg(2)	94.27(3)	Se(3)#1–Hg(2)–Se(4)	112.47(3)
C(31)–Se(3)–Hg(2)#1	106.8(3)	Se(2)–Hg(2)–Se(4)	108.39(3)
C(31)–Se(3)–Hg(1)	96.2(3)	S–Hg(3)–Se(4)	105.87(3)
Hg(2)#1–Se(3)–Hg(1)	98.02(3)	S–Hg(3)–Se(5)	97.20(3)
C(41)–Se(4)–Hg(3)	94.1(3)	Se(4)–Hg(3)–Se(5)	121.10(3)
C(41)–Se(4)–Hg(2)	105.8(3)	S–Hg(3)–Se(6)	100.975(14)
Hg(3)–Se(4)–Hg(2)	95.71(3)	Se(4)–Hg(3)–Se(6)	112.61(3)
C(51)–Se(5)–Hg(4)	106.4(3)	Se(5)–Hg(3)–Se(6)	114.93(3)
C(51)–Se(5)–Hg(3)	104.6(3)	O(1S)–Hg(4)–Se(6)#1	96.29(18)
Hg(4)–Se(5)–Hg(3)	91.23(3)	O(1S)–Hg(4)–Se(5)	105.5(2)
C(61)–Se(6)–Hg(4)#1	106.3(3)	Se(6)#1–Hg(4)–Se(5)	123.60(3)
C(61)–Se(6)–Hg(3)	105.3(3)	O(1S)–Hg(4)–Se(1)	98.6(2)
Hg(4)#1–Se(6)–Hg(3)	87.67(3)	Se(6)#1–Hg(4)–Se(1)	116.10(3)
Hg(1)#1–S–Hg(1)	103.77(6)	Se(5)–Hg(4)–Se(1)	111.16(3)
Hg(1)#1–S–Hg(3)#1	105.315(9)	C(1S)–O(1S)–Hg(4)	129.4(7)
Hg(1)–S–Hg(3)#1	111.630(9)	Se(7)–Hg(1)–Se(2)	110.09(5)
Hg(1)#1–S–Hg(3)	111.630(9)	Se(7)–Hg(1)–Se(3)	102.01(2)
Hg(1)–S–Hg(3)	105.315(9)	Se(2)–Hg(1)–Se(3)	113.49(3)
Hg(3)#1–S–Hg(3)	118.33(7)	Se(7)–Hg(1)–Se(1)	100.86(5)
		Se(2)–Hg(1)–Se(1)	116.72(3)

#1 = −x + 1, y, −z + 1/2.

strong intensity band at 2096 cm^{-1}. The spectrum of **1** also displays a ν(C=O) band at 1638 cm^{-1} absorption bands due to the dmf molecules present in the cluster.

Compound **1** and **2** were isolated as co-product from the same reaction, performed in dmf solvent. Firstly, **1** was obtained after 15 days as a crystalline. Single crystals of the polymeric compound **2** were obtained 5 days later. Compound **1** may be obtained at r.t as well as at 4 °C but **2** is isolated immediately afterward. Decomposition was observed at higher temperatures (40, 80 and 100 °C) and not reaction was observed at lower temperatures (−20 °C).

Compound **2** is the only product isolated when the reaction is performed in the presence of 2bpytm and, consequently, in a higher yield than in the absence of 2bpytm. Moreover, the reaction time is noticeably shortened.

In previous work we observed that secondary ligands such as 2bpytm are able to stabilize the intermediary PhSeHgX (X = Cl, Br, I) [20] formed initially- in coordination solvents- according to the reaction represented in Scheme 2 to afford polymeric cages. However, the exact role of secondary ligands in the assembly of the polymeric compounds is not yet identified.

Surprisingly, the central atom of the cluster **1** is a sulfur atom and consequently it means sulfurization and spontaneous self-assembly processes. The formation of S^{2-} and CN^{-} from SCN^{-} by oxidants and mediated for metals were documented by Schug and co-workers previously. Although thiocyanate was identified as sulfur source before [22], the mechanism responsible for the C–S cleavage is poorly understood and several different pathways have been proposed [23]. It is noteworthy the role of the aprotic

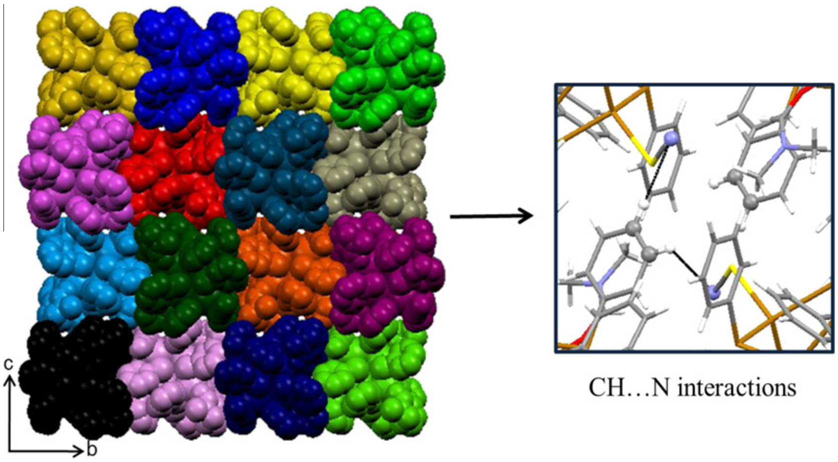

Fig. 2. View of the supramolecular organization in **1** showing details of the CH···N interactions along de *c* axis.

Table 3
Selected bond lengths (Å) and angles (°) for **2**.

Distances			
C(7)–N	1.157(7)	S(1)–Hg(1)	2.601(2)
C(7)–S(1)	1.661(9)	Se(1)–Hg(1)	2.5459(8)
N–Hg(1)#1	2.459(8)	Se(1)–Hg(1)#2	2.6038(9)
Angles			
C(7)–S(1)–Hg(1)	98.6(5)	Se(1)–Hg(1)–Se(1)#3	139.42(5)
C(1)–Se(1)–Hg(1)	101.2(3)	N(1)–Hg(1)–S(1)	95.4(3)
C(1)–Se(1)–Hg(1)#2	102.8(3)	Se(1)–Hg(1)–S(1)	119.71(9)
Hg(1)–Se(1)–Hg(1)#2	95.37(4)	Se(1)#3–Hg(1)–S(1)	95.65(8)

#1 = −x + 1,−y,−z; #2 = x,−y + 1/2,z + ½; #3 = x,−y + 1/2,z − 1/2.

coordinative solvent molecules for obtaining single crystals. of the stable cluster (Fig. 1).

Reaction with $Hg(SCN)_2$ differs from the analogous halides in several respects. Firstly, the bitopic character of the SCN^- makes possible the coordination through both the nitrogen and the sulfur atoms. Although, the tetrahedral mercury complexes are almost always S-bonded [7], the bridge coordinative mode in **2,** leads to the less common tetrahedral N-bonded. Moreover the free nitrogen atoms in **1** offer the possibility to increase the dimensionality of the compound through weak interactions. In fact, CH···N interactions are responsible for the supramolecular arrangement in the cluster (*vide infra*).

The free N atom and the nature of thiocyanate ligand with the variety of bonding modes (terminal as well as bridging) encourage us to use this cluster as building block for the synthesis of new compounds. The use of acceptor metal centers could give rise to new ternary compounds through the bound to the free nitrogen atom. In these sense, various synthetic attempts involving the use of the cluster as building block have been unsuccessful. In fact, when equimolar mixtures of $Hg(SCN)_2$ and $Hg(PhSe)_2$ were reacted with nickel(II) and manganese(II) chlorides the compound $[Hg_5Cl_3(PhSe)_7]$ [20] was always isolated, however $[Hg_8SeCl_4(PhSe)_{12}][Co(dmf)_6]$ [2] was obtained when the cobalt(II) salt was used. Formation of these compounds argues against the existence of the cluster compound in dmf solution.

4. Structural studies

4.1. Cluster compound 1

The compound **1** crystallizes in the orthorhombic space group *Pbcn*. The structure is similar to other compounds with the formula $[M_8E(EPh)_{12}X_4]^{2-}$ (where X = anion) studied before [1,24]. Chalcogenide clusters with mercury are rare and **1** is, to the best or our knowledge, the only neutral complex with the general formula $[M_8E(EPh)_{12}X_4]$ (X = anion or solvent). In this compound coexists a sulfido ligand with selonolate ones. Moreover two thiocyanate anions and two dmf solvent molecules are present in the molecular structure.

A central sulfur atom linked in a tetrahedral environment to four mercury atoms constitutes the core of the cluster (Fig. 1 right). Refinement of the structure including the central atom as selenium or disordered model (with different S/Se occupancies) were unsuccessful. Each of these four inner mercury atoms is bound, through three double bridging $SePh^-$ ligands (Se1 to Se6) to outer mercury atoms (Hg2 and Hg4), which also form a tetrahedron. So that, the eight mercury atoms as well as the central sulfur atom have a distorted tetrahedral coordination sphere (Table 2). In addition, Hg2 is bound to a sulfur atom of the thiocyanate ligand and Hg4 is bound to an oxygen atom belonging to a dmf solvent molecule. This kind of structure has been described as *centro-S-tetrahedro-Hg-icosaedro-(μ-SePh)$_{12}$-tetrahedro-tetrahedro-Hg-tetrahedro-(SePh)$_4$* or as well as four Hg inside and four Hg outside the triangular faces of an $(Se)_{12}$ icosahedron [24] and the eight mercury atoms bridge the triangular faces. Hg–S distances in the central sulfur atom are approximately 0.1 Å shorter than the Hg–Se distances (Table 2).

Each cluster stacks with adjacent ones through weak intermolecular CH…N hydrogen bonds that furnishing a 3D supramolecular architecture (Fig. 2). The thiocyanate molecules are essential for

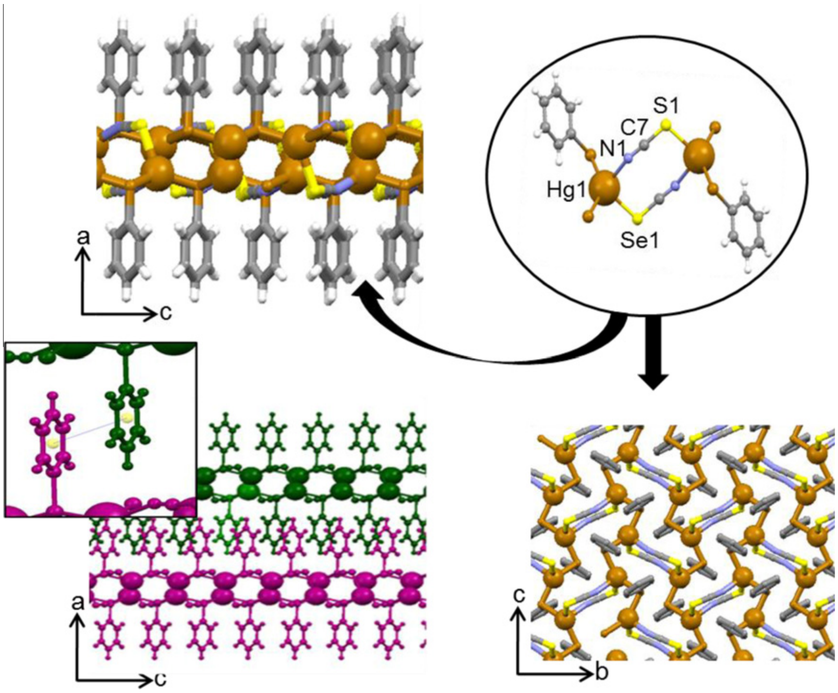

Fig. 3. 2D layer of [Hg(SCN)(SePh)] **(2)** showing in detail the $(Hg_2S_2C_2N_2)$ core together with a representation in the *bc* plane and the sandwich-like fashion. View in the *ac* plane of the 3D architecture in **2** showing details of the π–π stacking interactions.

the formation of the final organization due to two CH···N weak interactions with a C···N distances of 3.32 and 3.66 Å. In this way the molecules are not packed very efficiently, as evidence by the calculated density of 2.765 mg m^{-3} and the packing index [25] of 67%.

Whereas it is clear the role of the thiocyanate ligand in the supramolecular arrangement, solvent molecules do not take part in the supramolecular arrangement of the cluster.

*4.2. Polymeric compound **2***

Selected interatomic distances and angles are listed in Table 3 and the coordination environment of the mercury atom is shown in Fig. 3, together with the numbering scheme used. The compound is a 2D coordination polymer that crystallizes in the monoclinic $P2_1/c$ space group. The layers are formed by 8-membered metallocycles ($Hg_2S_2C_2N_2$) bounded to others by means of four $PhSe^-$ units along the *ac* plane. The construction of these macrocycles is based on the combination of two angular coordination mercury environments and two linear thiocyanate ligands. Mercury and selenium atoms form zig-zag chains along the *c* axis with the phenyl rings point alternately, up and down. The double thiocyanate ligands are responsible to link these chains along the *b* axis (Fig. 3). The layer can be described as a sandwich-like structure with an organometallic core forming by selenium, mercury and thiocyanate units and the organic phenyl groups pointed out the layer (Fig. 3).

Two SCN^- anions bridge two mercury(II) ions *via* N and S atoms (mode κ*S*:κ*N*) with bond distance of Hg–N = 2.459(8) Å and Hg–S = 2.604(9) Å. In most of the mercury (II) thiocyanate compounds the Hg–S distance is clearly shortly than the Hg–N distance [26]. There is only one example reported in the CSD database where the (μ)κ*S*:κ*N* double bridge thiocyanate ligands present bigger Hg–S distances (2.512; 2.589 Å) than Hg–N distances (2.465; 2.536 Å) [27]. The Hg···Hg separation due to the SCN-bridge is 5.887 Å, whereas de Hg···Hg distance through selenium atom is 3.809 Å.

The mercury metal center has a coordination number of four and the environment is a distorted tetrahedral with a Se_2NS coordination sphere, with the Hg–Se distances around the typical value of 2.5–2.6 Å (Table 3).

In analog halide coordination polymers, the supramolecular arrangement was made by means of CH···X interactions (X = Cl, Br). In **2**, this kind of interaction is not possible and only a very weak CH···S interaction is observed. The C···S distance is 3.899 Å and the C–H–S angle is 164° involving the –CH group of phenyl rings and sulfur atoms belonging to neighboring thiocyanates. In any case, this weak interaction reinforced the π–π stacking interaction, responsible for the 3D supramolecular array (Fig. 3). The adjacent layers are packed along the *a* axis through π–π stacking interactions (Fig. 3) involving [C1/C2/C3/C4/C5/C6] phenyl rings in a face-to-face mode (centroid-to-centroid distance is 3.729(7) Å and the interplanar dihedral angle is 0°).

In this case the aprotic solvent is essential to obtain single crystals but do not take part in the structure of the compound. The polymeric compound presents a packing Kitaigorodskii index [25] of 71.3%, a value that is greater than the index calculated for the previous cluster compound.

5. Conclusion

The reaction of $Hg(SePh)_2$ with $Hg(SCN)_2$ allows the isolation and structural characterization of the new binary cluster $[Hg_8S(SCN)_2(SePh)_{12}(dmf)_2]$ (**1**) and the 2D coordination polymer [Hg(SCN)(SePh)] (**2**). Synthesis conditions such as solvent or temperature has proved to be essential for the stabilization of both compounds. Thiocyanate ligand shows a different but crucial role; In **1**, is responsible for the supramolecular organization of the cluster and in **2**, is co-responsible for the polymerization of the compound but, do not take part in the supramolecular array. **2** is synthesized in less time and with high yield when 2bpytm molecule was used.

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Appendix A. Supplementary data

CCDC 838439 and 838440 contains the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2012.06.015.

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