Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Costero, Ana M. , Andreu, Cecilia , Monrabal, Elena , Tortajada, Amparo , Ochando, Luis E. and Amigó, José M.(1998) 'Bis-cyclic Crown Ether Derived from Biphenyl. Different Behaviour in Complexing $Hg(SCN)_2$ and $Hg(CN)_2$', Supramolecular Chemistry, 9: 3, 211 — 219

To link to this Article: DOI: 10.1080/10610279808034989

URL: http://dx.doi.org/10.1080/10610279808034989

SUPRAMOLECULAR CHEMISTRY, Vol. 9, pp. 211–219
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Bis-cyclic Crown Ether Derived from Biphenyl. Different Behaviour in Complexing $Hg(SCN)_2$ and $Hg(CN)_2$

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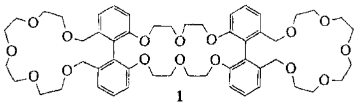
(Received 28 October 1997; In final form 23 February 1998)

A new bis-cyclic crown ether containing a biphenyl unit in its structure has been prepared. This compound shows unexpected behaviour in complexing $Hg(CN)_2$. The new ligand transports this mercury salt across liquid membranes with great efficiency. Clear differences have been observed in the complexation of $Hg(CN)_2$ and $Hg(SCN)_2$. The X-ray structure of a 1:2 mercury complex with $Hg(SCN)_2$ is also reported.

Keywords: Mercury complex, crown ethers, biphenyl, allosteric behaviour, transport

INTRODUCTION

Over the last few years, our research group has been involved in the synthesis of polycyclic crown ethers containing biphenyl units in their structures. The rigidity of the biphenyl-like system originates a transmission of conformational information between the complexing subunits which gives rise to allosteric behaviour in complexation [1]. Some ligands which show allosteric behaviour have been shown to be efficient carriers in transport experiments [2]; for this reason the final purpose of all these studies was to determine how allosteric cooperativity influences the transport of neutral species across liquid membranes. The compounds previously studied [3], **1**, **2**, and **3** had been shown to have limited efficiency in transport experiments (for different reasons in each case).



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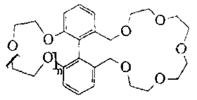

2 n=1
3 n=3
4 n=4

Here, we report the synthesis of a new compound, **4**, which surprisingly shows positive or negative allosteric cooperativity depending on the mercury salt ($Hg(SCN)_2$ or $Hg(CN)_2$) used in the complexation. Compound **4** was prepared from 6,6′-dihydroxy-2,2′-biphenyl-19-crown-5 (**5**) [3a] using standard procedures. In

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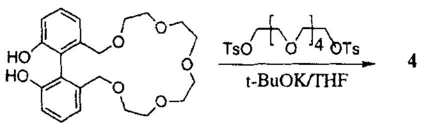
* Corresponding author.

contrast to compound **3**, in which only the benzylic subunit had an appropriate size for complexation, the size of each cavity in **4** was big enough to coordinate the mercury atom of both $Hg(SCN)_2$ and $Hg(CN)_2$. Complexation studies using ^1H NMR allowed us to establish the presence of one 1:1 complex and the only 1:2 complex, even though another 1:1 complex could be formed. In the observed 1:1 complex, the mercury atom was inside the phenolic cavity. The presence of the mercury atom in the phenolic cavity was detected because the complexation in this cavity shifted a signal downfield. This signal corresponded to one hydrogen of each methylene group which was directly bound to the phenolic oxygen. In addition, the signals corresponding to the benzylic moiety remained almost unchanged. In contrast, in the 1:2 complex, not only were modifications observed in the signals corresponding to the phenolic cavity, but the signal of the benzylic hydrogens also experimented significant changes.



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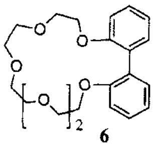
RESULTS AND DISCUSSION

Complexation Experiments

TABLE I Association constants of $Hg(SCN)_2$ and $Hg(CN)_2((CD_3)_2CO, 25°C)$

	$Hg(SCN)_2$	$Hg(CN)_2$
4	$K_1 = 1536$ $K_2 = 316$	$K_1 = 9903$ $K_2 = 179$
6	$K = 5567$	$K = 3428$
7	$K = 2700$	$K = 516$

Complexation experiments with **4** and the corresponding monocyclic counterpart **6** [4] and **7** [3a] were carried out in $(CD_3)_2CO$. The association constants which were determined using ^1H NMR, are reflected in Table I. From these data, it is possible to affirm that monocyclic compound **6** gives rise to a stronger complex than **7**, not only with $Hg(SCN)_2$, but also with $Hg(CN)_2$. This behaviour could be explained in different ways. First, the number of oxygen atoms that can be involved in complexation was higher in the phenolic compound, **6**, than in the benzylic one, **7**. In addition, the absence of supplementary substituents on the aromatic ring would allow the donor atoms to adopt the most suitable conformation for complexing. On the other hand, both ligands, **6** and **7**, complexed $Hg(SCN)_2$ with higher association constants than $Hg(CN)_2$. This could be due to the fact that the thiocyanate groups are less electronegative. In relation to this fact, Rebek [5] had previously shown that the higher electronegativity of the group bound to the mercury atom, the lower the association constant observed.



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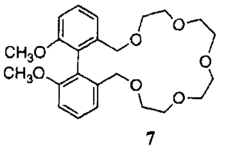

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In the corresponding bicyclic compound, **4**, the association constants calculated for $4 \cdot Hg(SCN)_2$ were easily understandable. Thus, complexation in the phenolic cavity (K_1) always gave rise to higher association constants than those observed in the benzylic subunit (K_2). In addition, both constants K_1 and K_2 were lower than K and K' respectively which agrees with studies previously carried out with related ligands that have shown that monocyclic compounds always give rise to a stronger complex than bicyclic ligands in mercury salts complexation [3, 7]. In that sense, the difference of values between the association constant monocyclic and bicyclic ligands could be due to the presence of a second crown ether in **4**. The presence of the new ring could prevent the oxygens in the cavity for adopting the most suitable conformation for binding the mercury atom.

For all the reasons given above, the high value of $K_1 = 9903$ for the complex **4** · $Hg(CN)_2$ was particularly surprising. A reason for this could be found in a higher sterical hindrance in $Hg(SCN)_2$ than in $Hg(CN)_2$ complexation. As explained above, bicyclic ligands present greater difficulties for adopting the most suitable conformation for binding the mercury atom, so the smaller cyanide group could be more easily packed.

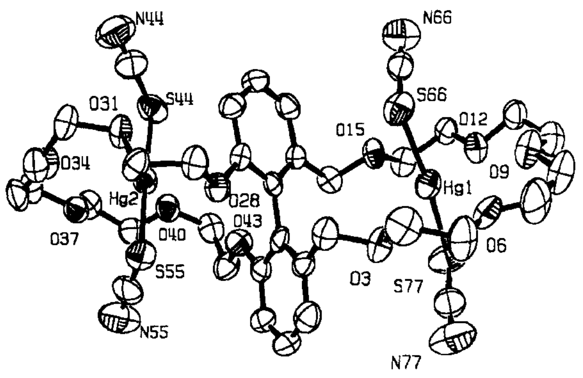


FIGURE 1A View of the molecular structure with crystallographic numbering scheme.

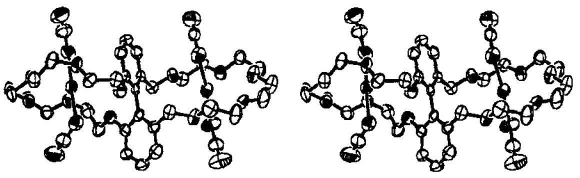


FIGURE 1B Stereoscopic view of its crystal packing of complex **4** · $[Hg(SCN)_2]_2$.

Structural Studies

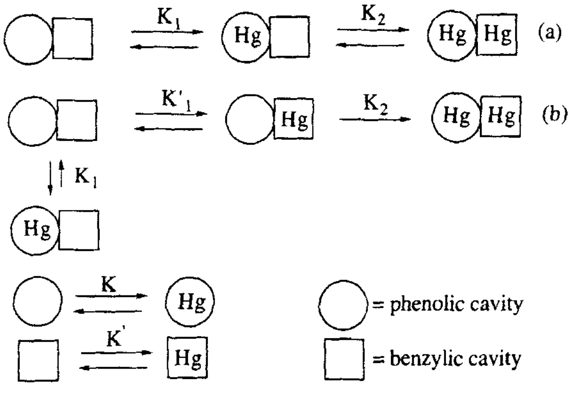
The 1:2 complex, **4** · $Hg(SCN)_2$, were crystallized and studied using X-rays. It contained two mercury atoms, one in each cavity. In the benzylic subunit, all the ethereal atoms participated in the coordination of the mercury. Four oxygen atoms in the ring were, on average, 0.009 Å from the oxygen mean plane. Disorder was found in the fifth oxygen. In the complex, the mercury atom was lying at approximately the oxygen mean plane and occupying a central position within the cavity. The Hg-O coordination length was not exceptional at 2.816 Å. Thus, in this cavity, the Hg atom was coordinated equatorially using five oxygen atoms. This resulted in a polyhedral coordination which is best described as a distorted pentagonal bipyramidal which involves both sulphur atoms.

By comparing the present structure with complexes previously studied [3, 6] it is possible to establish that the benzylic complex in this compound is more similar to that observed in **2** · $Hg(SCN)_2$ than in **3** · $Hg(SCN)_2$. In both **2** · $Hg(SCN)_2$ and **4** · $[Hg(SCN)_2]_2$, a distortion of the crown chain was observed. Thus, in the complex studied an opening of the C —C —O angles was noticed from C(7) to C(10). As a consequence, the torsion angle around C(7) —C(8) bond decreased from values which were close to 70° to values of around 11°. Thus, this new complex showed a difference in shape with that observed in **3** · $Hg(SCN)_2$ [3]. The results described suggest that the presence of some restrictions in the phenolic cavity (a very small ring as in the case of **2** or a complex as in the 1:2 complex of **4**) induces a loss of symmetry in the benzylic subunit.

With respect to the phenolic cavity, some interesting conclusions were obtained based on the X-ray data. First, the distance Hg(2)—O(31) was unusually long and the C —O —C angles were somewhat longer than tetrahedral. In addition, the torsion angles around O(31)—C(32) and O(40)—C(41) decreased from antiperiplanar to anticlinal conformation which was different from the opposite part of the phenolic crown. In any case, the six oxygen atoms were involved in the coordination of the mercury atom and they were, on average, 0.004 Å from the oxygen mean plane. In the phenolic complex, the metal atom was also lying at approximately the oxygen mean plane and, as expected, the Hg—O coordination length was larger (3.068 Å) than that observed in the benzylic subunit. The geometry can be considered as a distorted hexagonal bypiramidal that involves both sulphur atoms.

Allosteric Behaviour

Our interest in these studies was directed toward the influence that one subunit has on the ability of the second one in complexing the mercury salt. Thus, the first point was to establish which subunit acted as active and which as allosteric centre because in compound **4** both subunits were different. Two complexation schemes could be considered; in the first one (a), the phenolic cavity would act as allosteric centre and in the second (b), it would be the benzylic subunit which developed this role. The fact that the complex 1:1 containing the mercury atom in the benzylic cavity has never been observed in our experiments, allows us to propose mechanism (a) as the most probable in this process. If mechanism (b) were working, when 1 equivalent of the mercury salt was added, only the 1:2 complex would have been observed as a consequence of the almost irreversible formation of this 1:2 complex. However, when the experiment was carried out, a mixture of complex 1:1 and 1:2 were present which was in accordance with mechanism (a).



To verify whether **4** showed allosteric cooperativity, the Hill plot was used. When $Hg(SCN)_2$ was studied, data over the range of 30–70% saturation allowed us to determine a slope which was close to 1.9 which means a strong positive allosteric cooperativity. For this reason, only the 1:2 complex could be isolated. It was possible to establish that $K_1^i = 229$ and $K_2^i = 21$ from the slope value.

In the case of $Hg(CN)_2$, these titration experiments could not be done in acetone because there were some solubility problems. Titration experiments were carried out using methanol as a solvent and this allowed us to calculate a value of -0.36 for the slope of the Hill plot. This value indicates a clear negative allosteric cooperativity. The opposite behaviour of **4** in complexing both mercury salts could be due to the use of different solvents in the titration experiments. However, some qualitative experiments carried out in acetone seem to support the idea that certain characteristics of the mercury salt are more important than the influence of the solvent.

Transport Experiments

Transport of $Hg(CN)_2$ through a chloroform liquid membrane with **4** and a control experiment with an equimolecular mixture of **6** and **7** were examined in a U-tube. An aqueous solution of $Hg(CN)_2$ was placed in the left arm of the tube and atomic absorption analysis was used to determine the transport to the right arm. When the experiments were carried out under the same conditions, the transport efficiency of **4** was around 40% higher than that of the control mixutre when equal molar concentrations of holes were considered.

Thus, compound **4** provided a much more efficient transport across liquid membranes than similar compounds previously studied [3a,7]. The negative allosteric cooperativity observed in the complexation of $Hg(CN)_2$ by **4** seems to be responsible for this more efficient transport. Probably only the benzylic cavity is involved in transport and the phenolic one acts as the activator center that induces a very easy release of the mercury salt at the receiving phase.

It would have been very interesting to have carried out the same experiment using $Hg(SCN)_2$. This experiments would allow us to determine the influence of the positive allosteric cooperativity shown by **4** in the transport of the salt. Unfortunately, this transport experiment could not be carried out due to some solubility problems.

EXPERIMENTAL SECTION

NMR spectra were recorded in a Bruker AC-250, Varian Unity-300 and 400 spectrometers. Chemical shifts were reported in parts per million downfield from TMS. Residual solvent or TMS was taken as a reference.

Compounds **2**, **3**, **5**, **6**, and **7** were obtained as previously described in the literature [1-3]. All of them were fully characterized.

Synthesis of Macrobicycle 4

6,6′-dihydroxy-2,2′-biphenyl-19-crown-5 **(5)**, 111 mg(2.75 10^{-4} mol), and t-BuOK, 185 mg(1.65 10^{-3} mol) were dissolved in 50 ml of dry THF. The solution was stirred under argon atmosphere and heated under reflux for 1 day. Then, an additional portion of dry THF, 50 ml, was added. After the reflux temperature was again reached, a solution of pentaethylene glycol ditosylate (2.75 10^{-4} mol) in 50 ml of dry THF was added through a thin tube using a precision pump with continuous stirring and heating, as slowly as possible (around 5 h). The reaction mixture was refluxed with stirring for 60 h. After this, the THF was removed and then, dichloromethane, 30 ml, was added to the obtained solid. The organic phase was washed with aqueous NaOH (10%, 3 x 15 ml) and water (2 x 15 ml) and dried ($MgSO_4$). Removal of the solvent produced an oil which was purified by silica gel column chromatography (ethyl acetate: methanol from 9:1 to 6:4) to give 50 mg (30.0%) of clear oil. 300MHz ^1H NMR ($(CD_3)_2CO$) δ 7.31 (1H, t, J=7.8Hz), 7.18 (1H, dd, J_1=7.8Hz, J_2=1.2Hz), 7.01 (1H, d, J=7.8Hz), 4.17 (2H, s), 4.09 (1H, ddd, J_1=10.8Hz, J_2=7.2 Hz, J_3=3.3Hz), 3.97 (1H, dt, J_1=10.8Hz, J_2=4.5Hz), 3.71-3.92 (16H, m). 50MHz ^{13}C NMR ($CDCl_3$) δ 155.76 (s), 138.96 (s), 128.22 (d), 124.70 (d), 120.60 (s), 111.76 (d), 70.90 (t), 70.84 (t), 70.72 (t), 70.52 (t), 70.47 (t), 70.26 (t), 69.87 (t), 69.42 (t), 68.90 (t). Exact mass calcd. 606.3040, found 606.3039.

Synthesis of 4·*Hg(CN)$_2$*

1 equiv. of $Hg(CN)_2$ in acetone was added to 1 equiv. of **4** in acetone. The solution was stirred for 4 h and the solvent evaporated to give the 1:1 complex as a white solid. m.p. 235-236°C. 250MHz ^1H NMR ($CDCl_3$) δ7.44 (1H, t, J=7.9Hz), 7.36 (1H, d, 7.9Hz), 7.05 (1H, d, J=7.9Hz), 4.49 (1H, t, J=9.9Hz), 4.14 (2H, s), 3.91-3.42 (18H, m). 50MHz ^{13}C NMR ($CDCl_3$) δ 154.84 (s), 142.64 (s), 137.34 (s), 129.26 (d), 123.73 (d), 122.26 (s), 111.52 (d), 70.49 (t), 70.25 (t), 70.03 (t), 69.90 (t), 69.48 (t), 69.36 (t), 66.86 (t).

Synthesis of 4· *[Hg(SCN)$_2$]$_2$*

2 equiv. of $Hg(SCN)_2$ in acetone was added to 1 equiv. of **4** in acetone. The solution was stirred for 4 h and the solvent evaporated to give the 1:2 complex. m.p. 192°C. 300MHz ^1H NMR ($(CD_3)_2CO$) δ 7.39 (1H, t, J=8.1Hz), 7.25 (1H, d, J=8.1Hz), 7.15 (1H, d, J=8.1Hz), 4.60-4.54 (1H, m), 4.22 (1H, dd, J=11.0Hz), 4.16 (1H, dd, J=11.0Hz), 4.01-3.97 (1H, m), 3.85-3.54 (16H, m). 50MHz ^{13}C NMR ($CDCl_3$) δ 155.31 (s), 137.42 (s), 129.04 (d), 123.40 (d), 122.73 (s), 116.53 (s), 115.19 (s), 111.75 (d), 70.54 (t), 70.21 (t), 70.12 (t), 69.69 (t), 69.45 (t), 67.36 (t).

Synthesis of 6·*Hg(CN)$_2$*

1 equiv. of $Hg(CN)_2$ in acetone was added to 1 equiv. of **4** in acetone. The solution was stirred

for 4 h and the solvent evaporated to give the 1:1 complex as a white solid. m.p. 183–184°C. 250MHz ^{1}H NMR ($CDCl_3$) δ 7.35 (1H, dt, $J_1=8.0$ Hz, $J_2=2.1$ Hz), 7.16 (1H, d, $J=8.0$ Hz), 7.12–6.97 (2H, m), 4.52–4.42(1H, m), 3.85–3.46 (9H, m). 50MHz ^{13}C NMR ($CDCl_3$) δ 155.34 (s), 143.25 (s), 131.20 (d), 128.98 (s), 128.75 (d), 121.52 (d), 115.15 (s), 70.48 (t), 70.03 (t), 69.84 (t), 69.71 (t), 69,00 (t).

Synthesis of **6** $\cdot$ *Hg(SCN)$_2$*

1 equiv. of $Hg(SCN)_2$ in acetone was added to 1 equiv. of **4** in acetone. The solution was stirred for 4 h and the solvent evaporated to give the 1:1 complex as a white solid. m.p. 199–202°C. 250 MHz ^{1}H NMR ($CDCl_3$) δ 7.32 (1H, dt, $J_1=7.5$ Hz, $J_2=1.8$ Hz), 7.16 (1H, d, $J=7.5$ Hz), 7.08–6.98 (2H, m), 4.45–4.39 (1H, ddd, $J_1=10.9$ Hz, $J_2=8.2$ Hz, $J_3=1.7$ Hz), 3.85–3.69 (9H, m). 50MHz ^{13}C NMR ($CDCl_3$) δ 155.83 (s), 131.46 (d), 129.20 (s), 128.68 (d), 121.58 (d), 116.12 (s), 115.26 (s), 70.47 (t), 70.38 (t), 70.12 (t), 69.31 (t).

Association Constant Determination. General Method

A known amount of the complex was dissolved in 0.6 ml of acetone-d$_6$ in a NMR tube. The reference standard (Me_4Si) was added, and the tube was capped with Teflon tape. The NMR spectra were recorded on a 400 MHz spectrometer at 298 K. A ratio R between free form and complex could be determined from the part of the spectra where different signals were observed for the different species in solution, and K values could be obtained from it.

Titration of 4 with Hg(SCN)$_2$

A solution of **4** in acetone-d$_6$ with a concentration of 0.01511M was prepared. Of this, 0.6 ml were placed in a NMR tube, and the solvent level was marked. A second solution was made in the same solvent with a $Hg(SCN)_2$ concentration of 0.02030 M. An initial spectrum was recorded, 50 μL of the second solution was added to the NMR tube, and the solvent level was reduced by evaporation to the mark on the tube. The spectrum was then recorded again. This procedure was repeated until the number of equivalents of $Hg(SCN)_2$ added was higher than the number of equivalents of the crown ether in the tube. The different spectra showed separate signals for the aromatic protons of the free and complex crown ethers. From the R values, ln (bound sites/free sites) was plotted against $\ln[Hg(SCN)_2]_{free}$ (Hill plot) and the slope value determined (slope = 1.93, correlation coefficient = 0.99). Intrinsic association constants were $K_1^i = 229, K_2^i = 21$.

Titration of 4 with Hg(CN)$_2$

Titration was carried out as shown above. A solution 0.01445 M of **4** in methanol-d$_4$ was titrated with a solution 0.02692 M of $Hg(CN)_2$. The calculated slope was −0.36 (correlation coefficient = 0.99) and $K_1^i = 257$ and $K_2^i = 6$.

Transport Experiments

Transport experiments were carried out in a 13-mm diameter U-tube. The left arm was occupied by 8 ml of an aqueous 0.057 M solution of the $Hg(CN)_2$, and in the right arm, only deionized water (8 ml) was placed. Both solutions were separated through 12 ml of a 1.6×10^{-3} M solution of the carrier in $CHCl_3$. The two necks were closed with a tap and the system was stirred (500 rpm) at 25°C for 70 h. After that, the salt concentration in the right arm was determined by atomic absorption and the transport efficacy was expressed as molar concentration of the transported species in the right arm/mol carrier. Each experiment was repeated at least three times, and the results reported were the average of the determinations. The standard deviation from the mean value among the data in each experiment was lower that 5%. Diffusion was determined through a blank experiment.

X-ray Structure Analysis

Information concerning crystallographic data collection and refinement for the 1:2 complex of **4** with Hg$(SCN)_2$ is summarized in Table II. Intensity measurements were made on an Enraf-Nonius CAD4 diffractometer using a single crystal of dimensions 0.38×0.30×0.05 mm. Graphite-monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71069$ Å) and ω-scan technique was used. Data collection was carried out at room temperature. Three reference reflections were measured every 2 hours as an intensity and orientation check and no significant fluctuation was noticed during the collection of the data. Lorentz-polarization and empirical absorption (Ψ scans) corrections were made. The crystal structure was solved by Patterson methods [8] using the SHELXS86 program and refined by full-matrix least-squares techniques [9] on $F^{2\cdot}$. The non-hydrogen atoms were anisotropically refined. A little disorder in the oxygen (6) was found in the refinement process. This has been included in Table III as O(6A) and O(6B) considering an occupancy factor of 50% for each one since this value was the best one. An average position for O(6) was used to do the drawings. The hydrogen atoms were geometrically constructed with the SHELXL93-program with fixed isotropic displacement parameters. Fractional atomic coordinates with standard deviations (in parentheses) and equivalent isotropic temperature factors U(eq) are shown in Table III.

Figure 1a shows the molecular structure of complex $\mathbf{4}\cdot[\mathrm{Hg(SCN)_2}]_2$. In order to see the crystal packing and contents in the unit cell,

TABLE II Crystal data and structure refinement for $\mathbf{4}\cdot[\mathrm{Hg(SCN)_2}]_2$

Empirical formula	$C_{36}H_{46}Hg_2N_4O_{11}S_4$	
Formula weight	1240.19	
Temperature	293(2) K	
Wavelength	0.71069 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 13.021$ (5) Å	alpha = 109.41 (3) deg.
	$b = 13.536$ (4) Å	beta = 106.56 (4) deg.
	$c = 14.582$ (6) Å	gamma = 106.213 (3) deg.
Volume	2115.5 (13) Å^3	
Z	2	
Density (calculated)	1.947 Mg/m^3	
Absorption coefficient	7.507 mm^{-1}	
F (000)	1204	
Crystal size	0.38×0.30×0.05 mm	
Theta range for data collection	1.63 to 25.00 deg.	
Index ranges	$-15 <= h <= 14$, $-16 <= k <= 15$, $0 <= l <= 17$	
Reflections collected	7640	
Independent reflections	7318 [R(int) = 0.0302]	
Refinement method	Full-matrix least-square on F^2	
Data / restraints / parameters	7314 / 0 / 523	
Goodness-of-fit on F^2	0.984	
Final R indices [$I > 2$ sigma(I)]	$R1 = 0.0423$, $wR2 = 0.0828$	
R indices (all data)	$R1 = 0.1034$, $wR2 = 0.0945$	
Largest diff. peak and hole	1.372 and -1.145 e.Å^{-3}	

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4** · [Hg (SCN)$_2$]$_2$ U(eq.) is defined as one third of the trace of the orthogonalized U_{ij} tensor. Oxygen (6) is included as O (6A) and O (6B) with an occupancy factor equal to 0.5 for each one, due to the disorder

	x	*y*	*z*	*U* (*eq.*)
Hg (1)	1754 (1)	3117 (1)	2832 (1)	52 (1)
Hg (2)	5411 (1)	8097 (1)	1996 (1)	52 (1)
S (44)	6456 (3)	7105 (2)	1326 (2)	69 (1)
C (44)	7745 (10)	7700 (10)	2394 (9)	73 (3)
N (44)	8644 (9)	8079 (11)	3061 (10)	116 (4)
S (55)	4306 (2)	9011 (2)	2639 (2)	64 (1)
C (55)	3630 (11)	9084 (9)	1632 (11)	80 (3)
N (55)	3043 (10)	9121 (10)	836 (10)	114 (4)
S (66)	3734 (2)	3796 (2)	4008 (2)	67 (1)
C (66)	4236 (8)	2997 (9)	3281 (8)	63 (3)
N (66)	4662 (9)	2471 (9)	2873 (8)	98 (3)
S (77)	−170 (2)	2568 (3)	1594 (2)	84 (1)
C (77)	−669 (9)	3316 (9)	2302 (9)	72 (3)
N (77)	−1119 (9)	3796 (9)	2755 (9)	114 (4)
O (3)	1842 (5)	5279 (5)	4222 (5)	62 (2)
O (6A)	1429 (9)	3324 (12)	4665 (12)	66 (4)
O (6B)	765 (25)	3207 (24)	4336 (23)	56 (7)
O (9)	1169 (6)	1249 (5)	3287 (5)	70 (2)
O (12)	1248 (5)	967 (4)	1317 (4)	55 (2)
O (15)	2523 (5)	2955 (4)	1172 (4)	49 (1)
O (28)	4798 (5)	7757 (4)	4095 (4)	51 (2)
O (31)	7072 (5)	9380 (4)	4538 (5)	55 (2)
O (34)	7240 (5)	10295 (5)	2963 (5)	56 (2)
O (37)	5587 (5)	9153 (5)	724 (5)	54 (2)
O (40)	4064 (5)	6789 (5)	−294 (4)	56 (2)
O (43)	2720 (5)	6161 (5)	857 (4)	54 (2)
C (1)	2164 (7)	6261 (6)	3175 (7)	45 (2)
C (2)	2692 (8)	6167 (7)	4176 (7)	55 (2)
C (4)	2174 (9)	5313 (9)	5264 (7)	76 (3)
C (5)	1243 (10)	4332 (8)	5210 (8)	79 (3)
C (7)	715 (12)	2392 (11)	4618 (10)	99 (4)
C (8)	616 (10)	1289 (9)	3974 (9)	85 (3)
C (10)	752 (9)	173 (8)	2436 (7)	67 (3)
C (11)	1437 (8)	235 (7)	1784 (7)	57 (2)
C (13)	1722 (7)	945 (6)	553 (7)	48 (2)
C (14)	1698 (7)	1906 (6)	275 (6)	50 (2)
C (16)	2632 (7)	3950 (6)	1018 (6)	45 (2)
C (17)	3726 (7)	4918 (6)	1903 (6)	39 (2)
C (18)	4755 (8)	4767 (7)	2037 (7)	52 (2)
C (19)	5829 (8)	5641 (8)	2879 (7)	54 (2)
C (20)	5845 (7)	6623 (7)	3559 (7)	49 (2)
C (21)	4847 (7)	6790 (6)	3450 (6)	39 (2)
C (22)	3753 (7)	5939 (6)	2608 (6)	35 (2)
C (23)	2673 (7)	6149 (6)	2450 (6)	41 (2)
C (24)	2146 (7)	6263 (6)	1516 (7)	45 (2)
C (25)	1181 (7)	6508 (7)	1334 (8)	56 (2)
C (26)	703 (8)	6607 (7)	2084 (9)	66 (3)
C (27)	1188 (8)	6483 (7)	2996 (8)	60 (3)
C (29)	5728 (7)	8509 (6)	5134 (6)	52 (2)
C (30)	6457 (7)	9611 (7)	5176 (7)	54 (2)
C (32)	7959 (8)	10413 (7)	4710 (7)	60 (3)
C (33)	7527 (8)	10983 (7)	4061 (7)	61 (3)
C (35)	6959 (9)	10842 (7)	2311 (8)	64 (3)
C (36)	6715 (9)	10074 (7)	1192 (8)	66 (3)
C (38)	5281 (8)	8416 (8)	−355 (7)	61 (3)
C (39)	4044 (8)	7501 (8)	−826 (7)	58 (2)
C (41)	2953 (8)	5833 (7)	−745 (7)	61 (3)
C (42)	2183 (7)	6086 (8)	−184 (7)	60 (3)

Figure 1b shows a stereoscopic view of the unit cells. Both figures were made with PLUTON [10]. A list of anisotropic displacement parameters for non-hydrogen atoms, bond lengths and angles, hydrogen atoms coordinates and tables of calculated and observed structure factors (F_O–F_C) have been deposited as supplementary material at the Cambridge Crystallographic Data Centre.

Acknowledgments

We thank the Dirección General de Investigación Científica y Técnica (PB92-0871) for its financial support for this research and the Generalitat Valenciana for a grant to E. Monrabal. L. E. Ochando also would like to thank the Generalitat Valenciana (PVCYT) for a postdoctoral fellowship. The authors are grateful to. J. Rius and M. Font (ICMAB-CSIC) for their help in data collection.

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