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Coordination chemistry of anticrowns: Complexation of cyclic trimeric perfluoro-*o*-phenylenemercury with nitro compounds

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Abstract

Cyclic trimeric perfluoro-*o*-phenylenemercury (o-C$_6$F$_4$Hg)$_3$ (**1**) is capable of reacting with nitromethane to give complex {[(o-C$_6$F$_4$Hg)$_3$](CH$_3$NO$_2$)} (**2**) containing one molecule of the nitro compound per one macrocycle molecule. In this complex, the nitromethane ligand is bound to **1** by its both oxygen atoms, one of which is simultaneously coordinated to all three Hg centres of the macrocycle while the other interacts with a single Hg centre. The complex of similar composition, {[(o-C$_6$F$_4$Hg)$_3$](C$_6$H$_5$NO$_2$)} (**3**), is produced in the interaction of **1** with nitrobenzene. In this complex too, the both oxygen atoms of the nitro group are involved in the bonding to the macrocycle. A distinctive feature of **3** is that here one oxygen atom of the coordinated nitro derivative is bound by only two Hg centres of **1** whereas the other interacts again with a single Hg site. The reaction of **1** with 5-nitroacenaphthene affords a 1:1 complex, {[(o-C$_6$F$_4$Hg)$_3$](C$_{12}$H$_9$NO$_2$)} (**4**), having a polydecker sandwich structure in the crystal. Unlike in **3**, the aromatic rings of the nitroarene units in **4** are disposed virtually in parallel to the macrocycles. The nitro compound in **4** behaves again as a bidentate ligand, forming three Hg–O bonds with one of the adjacent macrocycles and a single Hg–O bond with another molecule of **1**. The complex is characterized also by shortened Hg–C contacts between the Hg centres of **1** and the carbon atoms of the nitroarene moiety as well as shortened C–C contacts between the carbon atoms of the nitroarene and the macrocycle. In the interaction of **1** with 1-nitropyrene, complexes of two compositions, viz. {[(o-C$_6$F$_4$Hg)$_3$](C$_{16}$H$_9$NO$_2$)} (**5**) and {[(o-C$_6$F$_4$Hg)$_3$](C$_{16}$H$_9$NO$_2$)$_3$} (**6**) are formed. An X-ray diffraction study of **6** has shown that in this adduct two of three coordinated molecules of the nitro compound are located on one side of the metallacycle plane while the third nitroarene molecule is disposed on its other side. The aromatic rings of all three nitropyrene ligands in **6** are practically parallel to the mean plane of the macrocycle. In contrast to **2**–**4**, each molecule of the nitroarene in **6** is bonded to **1** by a single oxygen atom which is coordinated only to one Hg centre. In the case of one of the nitropyrene ligands that forms much longer Hg–O bond with **1** than two others, an additional contribution to the bonding is made by shortened Hg–C contacts between the macrocycle and the carbon atoms of the aromatic pyrene core and also by shortened C–C contacts between the carbon atoms of the coordinated nitroarene and **1**. The synthesized adducts are the first examples of complexes of an anticrown with nitro compounds.
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Keywords: Anticrowns; Complexes; Macrocyclic multidentate Lewis acids; Mercury; Nitro compounds; Polymercuramacrocycles

1. Introduction

Over the last two decades, there has been a rapid progress in host–guest chemistry of macrocyclic multidentate Lewis acids named anticrowns [1] because of their

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charge-reverse analogy with crown ethers and related compounds (see e.g. reviews [2a–f] and recent papers [3a–o]). The majority of studies in this important area has been conducted on polymercuramacrocycles which proved to be very efficient hosts for binding various anionic and neutral Lewis basic guests. The possibility of using such macrocycles in catalysis [2a–c,3e] and as ionophores for ion-selective electrodes [2b,3d] has also been demonstrated.

As part of our ongoing research into binding and catalytic properties of anticrowns, we have previously described a series of complexes of cyclic trimeric perfluoro-*o*-phenylen-emercury (o-$C_6F_4Hg)_3$ (**1**), containing three Hg atoms in a planar nine-membered ring [4], with different anionic species (Cl$^-$, Br$^-$, I$^-$, SCN$^-$, *closo*-[B$_{10}$H$_{10}$]$^{2-}$, *closo*-[B$_{12}$H$_{12}$]$^{2-}$, [Fe(CN)$_6$]$^{3-}$, [Fe(CN)$_5$(NO)]$^{2-}$, etc.) [2a,2c,3k]. The ability of **1** to coordinate neutral Lewis bases such as nitriles [2a,2c], carbonyl compounds [2a,2c,2d,3c], arenes [2d,3n], metallocenes [3i,3j], azulene [3a], 6-(*N,N*-dimethylamino) pentafulvene [3a], polyynes [3b], dimethyl sulfide [3o] and some others has also been established. In the majority of structurally characterized complexes, the molecule of a Lewis base is cooperatively bound by all Lewis acidic Hg sites of the macrocycle, thereby leading to the unusual pyramidal, bipyramidal and sandwich structures or fragments.
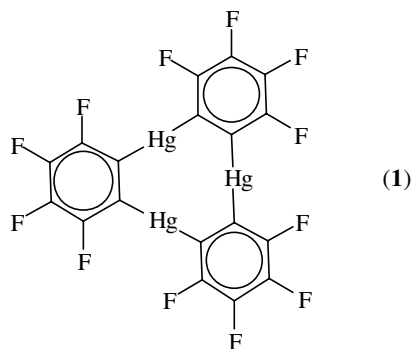
Another interesting feature of **1** is its capacity to transfer organic and inorganic cations from an aqueous phase to an organic phase which makes this macrocycle potentially useful for phase transfer catalysis of electrophilic reactions [2a,2c,3e]. Recently, we have reported a high activity of **1** in the phase transfer nitration of a number of aromatic substrates (2-methylnaphthalene, 1,3- and 2,6-dimethyl-naphthalenes, acenaphthene, anthracene, pyrene) with dilute nitric acid in the presence of sodium nitrite as an initiator and sodium chloride as a promoter [3e]. A detailed examination of the acenaphthene nitration catalysed by **1** revealed that the greatest reaction rates are observed on the use of a 1:1 benzene–nitrobenzene mixture as the organic phase. The replacement of the benzene–nitrobenzene mixture by benzene, in which the major part of the catalyst remains undissolved, leads to the appearance of an induction period on the kinetic curve and to a decrease

in the rate of the nitration. It should be noted, however, that by the end of the induction period all quantity of **1** dissolves completely in the benzene layer. Furthermore, when the resulting nitroacenaphthenes are introduced in the benzene phase before the reaction, the induction period practically disappears and the rate of the process correspondingly increases. These data could be explained by an enhancement in the solubility of macrocycle **1** in the organic phase due to its coordination with the Lewis basic oxygen atoms of the nitro group, which prompted us to investigate the complexation reactions of **1** with nitro compounds.

In the present article, we report the synthesis and structures of the complexes of **1** with nitromethane, nitrobenzene, 5-nitroacenaphthene and 1-nitropyrene. The synthesized compounds are the first examples of host–guest complexes of nitro derivatives with an anticrown.

2. Results and discussion

Complexes of **1** with nitromethane and nitrobenzene are readily formed under conditions of recrystallization of **1** from the corresponding nitro compound as a solvent. The isolated complexes are colourless crystalline solids stable to air. According to elemental analyses, the complexes can be formulated as {[(o-$C_6F_4Hg)_3$](CH$_3$NO$_2$)} (**2**) and {[(o-$C_6F_4Hg)_3$](C$_6$H$_5$NO$_2$)} (**3**), respectively, i.e., contain one molecule of a nitro compound per one macrocycle molecule. The complex of similar composition, {[(o-$C_6F_4Hg)_3$](C$_{12}$H$_9$NO$_2$)} (**4**), was isolated as an orange-yellow fine-crystalline solid from the interaction of **1** with an equimolar amount of 5-nitroacenaphthene in CH$_2$Cl$_2$. The use of a fivefold excess of the nitro derivative in this reaction leads to the same compound **4**. The IR spectrum of **2** in Nujol mull exhibits the v_{as}(NO) band of the coordinated nitro group at 1551 (m) cm^{-1} shifted by 13 cm^{-1} to a low-frequency region in comparison with the v_{as}(NO) band for neat nitromethane. The IR spectrum of **3** in Nujol displays the v_{as}(NO) band at 1507 (s) cm^{-1} as well as the v_s(NO) band at 1345 (s) cm^{-1} which are shifted by 17 and 3 cm^{-1}, respectively, to lower wave numbers relative to the corresponding bands in the spectrum of uncoordinated nitrobenzene. The IR spectrum of **4** contains the v_{as}(NO) bands at 1495 (m) and 1488 (m) cm^{-1} and the v_s(NO) band at 1310 (ms) cm^{-1}, which are shifted by 14–21 and 15 cm^{-1}, respectively, to lower frequencies relative to the corresponding bands (v_{as}(NO) = 1509 cm^{-1}, v_s(NO) = 1325 cm^{-1}) for free 5-nitroacenaphthene. The ^{199}Hg NMR spectra of **2**–**4** at 20 °C in THF (the initial concentration is 8×10^{-2} M) show only negligible differences from the spectrum of free **1** but the addition of an excess of a nitro compound (40:1) to a solution of the corresponding complex in THF leads to a noticeable downfield shift of the ^{199}Hg resonance (by 3–4 ppm in the case of **2** and **3** and by 8 ppm in the case of **4**).

Unlike the reactions with nitromethane, nitrobenzene and 5-nitroacenaphthene, the reaction of **1** with 1-nitropy-

rene affords complexes of two different compositions, viz. $\{[(o\text{-}C_6F_4Hg)_3](C_{16}H_9NO_2)\}$ (**5**) and $\{[(o\text{-}C_6F_4Hg)_3](C_{16}H_9NO_2)_3\}$ (**6**), containing one and three molecules of a nitro compound, respectively, per one molecule of the macrocycle. Complex **5** is formed in the interaction of **1** with an equimolar amount of 1-nitropyrene in CH_2Cl_2 and represents a fine-crystalline yellow powder. Complex **6** is obtained in the interaction of **1** with a threefold excess of 1-nitropyrene in a THF–CH_3OH mixture and represents a yellow-orange crystalline solid. An attempt to grow crystals of **5** from THF resulted in the formation of complex **6**. The IR spectrum of **6** (Nujol) is characterized by the $\nu_{as}(NO)$ and $\nu_s(NO)$ bands at 1501 (m) and 1305 (ms) cm^{-1} shifted by 9 and 25 cm^{-1}, respectively, to a low-frequency region as compared to the corresponding bands for free 1-nitropyrene ($\nu_{as}(NO) = 1510$ (s) cm^{-1}, $\nu_s(NO) = 1330$ (vs) cm^{-1}). The IR spectrum of **5** shows the same $\nu_{as}(NO)$ and $\nu_s(NO)$ bands as complex **6**. The ^{199}Hg NMR spectrum of **6** in THF ($[6]_0 = 8 \times 10^{-2}$ M), in contrast to the corresponding spectra of **2**, **3** and **4**, exhibits a noticeable downfield shift of the ^{199}Hg resonance (by 9 ppm) relative to that of starting **1** even in the absence of an excess of a nitro compound.

Fig. 1 shows the structure of complex **2**. Selected bond lengths and angles for **2** are given in Table 1. The complex occupies in the crystal a special position on a mirror plane passing through the Hg(1), O(1), O(2), N(1) and C(10) atoms and the mid-point of the Hg(2)···Hg (2A) line. The nitromethane molecule in the complex behaves as a bidentate Lewis base and forms two types of the Hg–O bonds with the macrocycle. As seen from Fig. 1, one of the oxygen atoms (O(1)) of the nitro group is cooperatively coordinated here by all three Hg centres of **1** whereas the other (O(2)) interacts with a single Hg centre. The Hg–O distances in **2** are close to each other (3.010(7)–3.078(8) Å) and are significantly shorter than the sum of the van der Waals radii of Hg (1.73–2.00 Å [5a,5b], 2.1 Å [5c]) and O (1.5 Å [5c], 1.54 Å [5d]) atoms. Unfortunately,

Fig. 1. Molecular structure of complex **2** in the crystal.

Table 1
Selected bond lengths (Å) and angles (°) in complex **2**

Hg(1)–O(1)	3.078(8)	N(1)–O(2)	1.211(12)
Hg(2)–O(1)	3.010(7)	C(10)–N(1)	1.477(13)
Hg(2A)–O(1)[a]	3.010(7)	Hg(1)–C(1)	2.081(8)
Hg(1)–O(2)	3.037(9)	Hg(2)–C(2)	2.061(8)
N(1)–O(1)	1.243(12)	Hg(2)–C(7)	2.068(7)
C(1)–Hg(1)–C(1A)[a]	172.7(4)	O(2)–N(1)–C(10)	119.0(9)
C(2)–Hg(2)–C(7)	176.7(3)	O(1)–N(1)–C(10)	118.3(9)
O(1)–N(1)–O(2)	122.7(9)		

[a] Symmetry transformation $x, -y + 3/2, z$ was used to generate equivalent atoms.

the limited accuracy of the X-ray experiment does not allow judgement on the influence of the complexation of nitromethane with **1** on the N–O bond lengths (the N–O distances in free nitromethane are 1.221(5) and 1.215(5) Å, av. 1.218 Å [6]). The O(1)O(2)N(1)C(10) plane of the nitromethane ligand is perpendicular to the mean plane of the central nine-membered mercuracarbon ring of **1**.

In the crystal, molecules of the complex are associated into infinite ladder-like chains (Fig. 2) due to shortened intermolecular Hg···F and Hg···C contacts (Hg···F 3.197(5) and 3.264(5) Å, Hg···C 3.536(7)–3.629(7) Å) between the neighbouring molecules of **2** ($r_{vdw}(F) = 1.4$ Å [5c], $r_{vdw}(C_{arom}) = 1.7$ Å [5c]). The chains are arranged along the a crystal axis. The distance between the mean planes of the central Hg_3C_6 rings of two adjacent macrocycles in each chain is 3.33 Å and the projections of their centroids onto the plane parallel to these cycles are shifted relative to each other by 5.88 Å. The formation of similar extended ladder-like chains with shortened intermolecular Hg···F and Hg···C contacts was previously observed in the crystal packing of the pyramidal 1:1 complex of **1** with acrylonitrile (Hg···F 3.35 and 3.42 Å, Hg···C 3.56 and 3.67 Å) [7] and the sandwich 2:2 complex of **1** with maleic anhydride (Hg···F 3.32 Å, Hg···C 3.42–3.63 Å) [3c]. In the latter case, the resulting chains are linked with one another through additional shortened intermolecular Hg···F contacts (3.22–3.48 Å).

The coordinated molecule of a nitro compound in **3**, as in **2**, behaves as a bidentate Lewis base and forms two types of the Hg–O bonds with **1** (Fig. 3). However, in the mode of the coordination of a nitro group with the macrocycle, complex **3** differs essentially from **2**: while one oxygen atom (O(2)) of a nitro derivative in **3** is bonded again to a single Hg centre of **1**, the other (O(1)) interacts only with two rather than three Lewis acidic Hg sites. The Hg–O bond distances in **3** vary over wider limits (2.858(6)–3.254(5) Å; see Table 2) than in **2** and all these separations are again substantially shorter than the corresponding van der Waals distance. The length of the N(1)–O(1) bond in **3** (1.235(7) Å) differs only insignificantly from that of the N(1)–O(2) bond (1.211(9) Å), both these distances being close to the N–O distances in uncoordinated nitrobenzene (1.223(5) and 1.229(5) Å, av. 1.226 Å [8]). An interesting
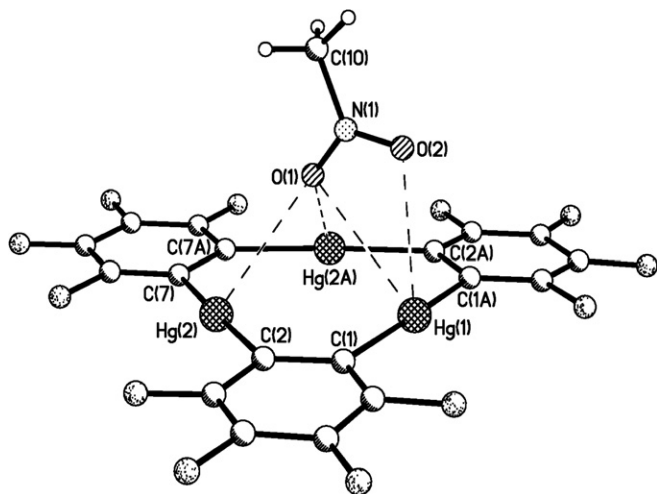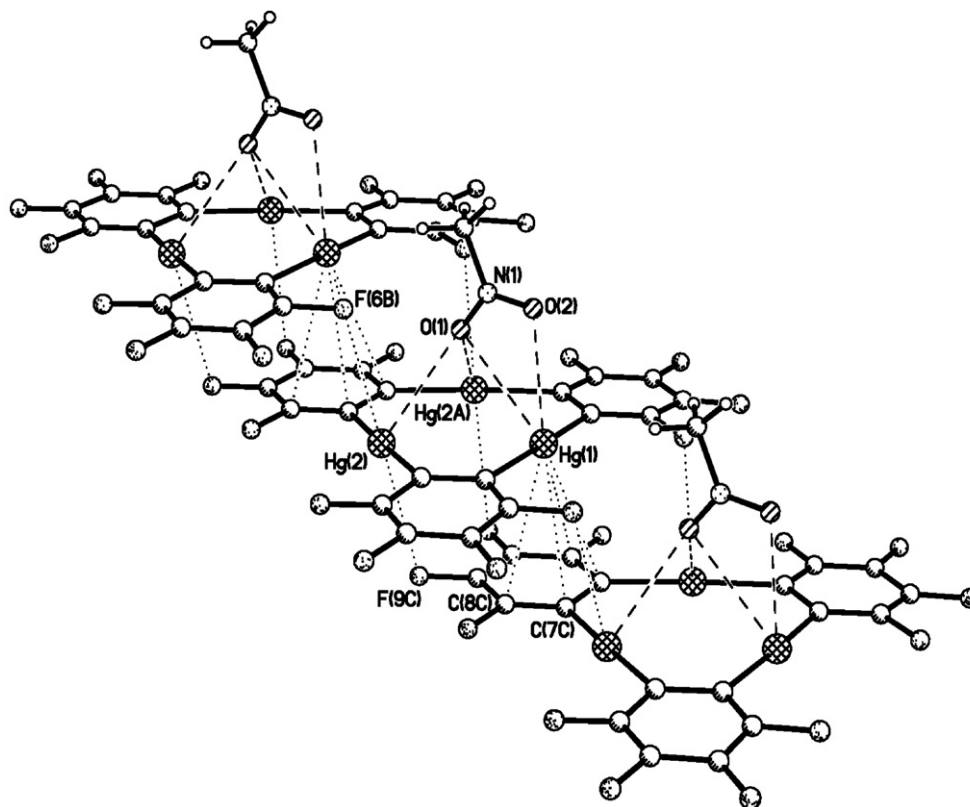
Fig. 2. View of a fragment of crystal packing of complex **2**, showing the shortest intermolecular Hg···F and Hg···C contacts between neighbouring molecules of **2**.

structural feature of complex **3** is a strong deviation of the oxygen atoms of the nitrobenzene ligand from its phenyl ring plane (the dihedral angle between the planes of the nitro group and the phenyl ring is 21.1°). In all other struc-

Fig. 3. Molecular structure of complex **3** in the crystal.

turally characterized nitrobenzene complexes with metal compounds, this deviation is considerably smaller (0.5–8.2°) [9]. As is known, free molecule of nitrobenzene has an essentially planar structure (the corresponding interplane angle is 2.1° [8]). The dihedral angles between the mean plane of the central nine-membered mercuracarbon cycle of **1** and the planes of the nitro and phenyl groups are 69.3° and 65.3°, respectively.

In the crystal, complex **3** forms cofacial dimers due to shortened intermolecular Hg···Hg (3.4675(7) Å) and Hg···C (3.536(6)–3.617(6) Å) contacts between the adjacent molecules of **3** (Fig. 4). The dimers are linked with one another through additional shortened Hg···F contacts (3.280(5) and 3.412(5) Å). In each of the dimers, the mutually parallel planes of the central Hg_3C_6 rings of the macrocycles are separated by 3.37 Å and the projections of
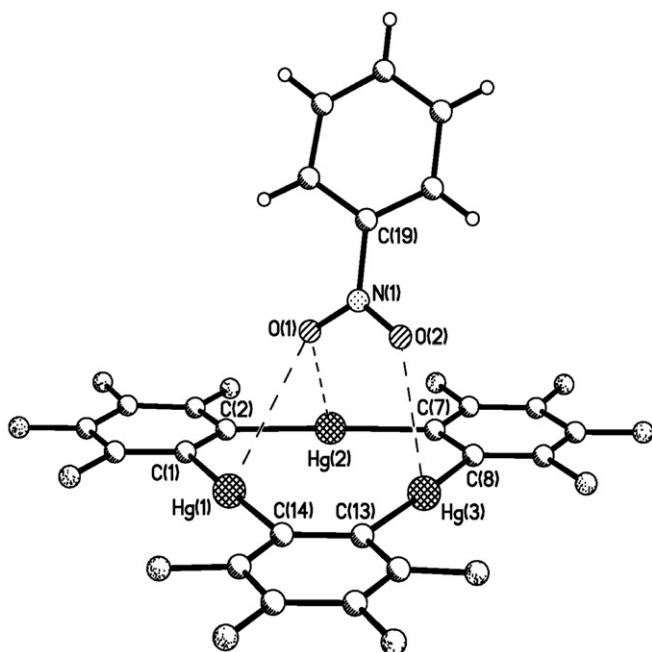
Table 2
Selected bond lengths (Å) and angles (°) in complex **3**

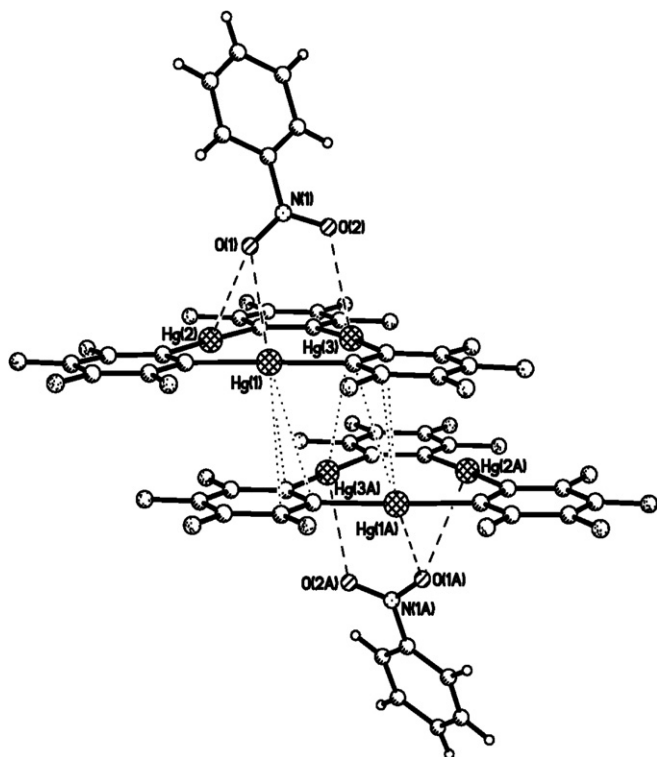|			
Hg(1)–O(1)	3.254(5)	Hg(1)–C(1)	2.075(6)
Hg(2)–O(1)	2.953(5)	Hg(1)–C(14)	2.062(6)
Hg(3)–O(2)	2.858(6)	Hg(2)–C(2)	2.080(7)
N(1)–O(1)	1.235(7)	Hg(2)–C(7)	2.076(6)
N(1)–O(2)	1.211(9)	Hg(3)–C(8)	2.071(7)
C(19)–N(1)	1.453(8)	Hg(3)–C(13)	2.078(7)
C(1)–Hg(1)–C(14)	176.9(3)	O(1)–N(1)–O(2)	121.2(7)
C(2)–Hg(2)–C(7)	176.1(3)	O(2)–N(1)–C(19)	119.0(6)
C(8)–Hg(3)–C(13)	175.3(3)	O(1)–N(1)–C(19)	119.8(6)

Fig. 4. View of the dimer of **3**, showing the shortest intermolecular Hg···Hg and Hg···C contacts between neighbouring molecules of **3**.

the centroids of the Hg_3C_6 macrocyclic units onto the plane parallel to these units are shifted with respect to one another by 3.00 Å. The mutual orientation of the neigh-

bouring macrocycles in the dimers corresponds to an eclipsed conformation. The formation of cofacial dimers was also observed earlier in the crystal packing of the pyramidal 1:1 complex of **1** with *n*-butyronitrile (Hg···Hg 3.372 and 3.512 Å, Hg···C 3.58 and 3.59 Å). These dimers are linked in the crystal with each other through additional shortened Hg···F contacts (3.28 and 3.44 Å) as well [10]. The pyramidal 1:1 complex of **1** with acetone is also associated in the crystal into cofacial dimers due to shortened intermolecular Hg···Hg (3.512 Å) and Hg···C (3.402 and 3.483 Å) contacts [11]. However, in this case, no shortened Hg···F contacts between the dimer units are observed.

In contrast to **2** and **3**, analogous in its composition complex **4** has a polydecker sandwich stucture in the crystal (see Fig. 5). Interestingly, the aromatic rings of the nitroarene units are disposed here virtually in parallel to the macrocycles (the interplane angle is 2.4°), however, the plane of the nitro group deviates from the aromatic ring plane of the nitroacenaphthene ligand by 33.7°. As in **2** and **3**, both oxygen atoms of the NO_2 group of the nitroarene in **4** are involved in the bonding to the anticrown molecules. As seen from Fig. 5, one of these oxygen atoms (O(1)) is simultaneously bound to all three Lewis acidic Hg sites of one of the adjacent macrocycles (Hg(1)–O(1) 3.069(5) Å, Hg(2)–O(1) 3.174(5) Å, Hg(3)–O(1) 3.345(5) Å, see Table 3) whereas the other oxygen atom (O(2)) coordinates with a single Hg centre of another molecule of **1** (Hg(3A)–O(2) 3.075(5) Å). The N–O distances in **4** are close to each other (Table 3). The complex is characterized also by the presence of shortened Hg–C contacts between the mercury
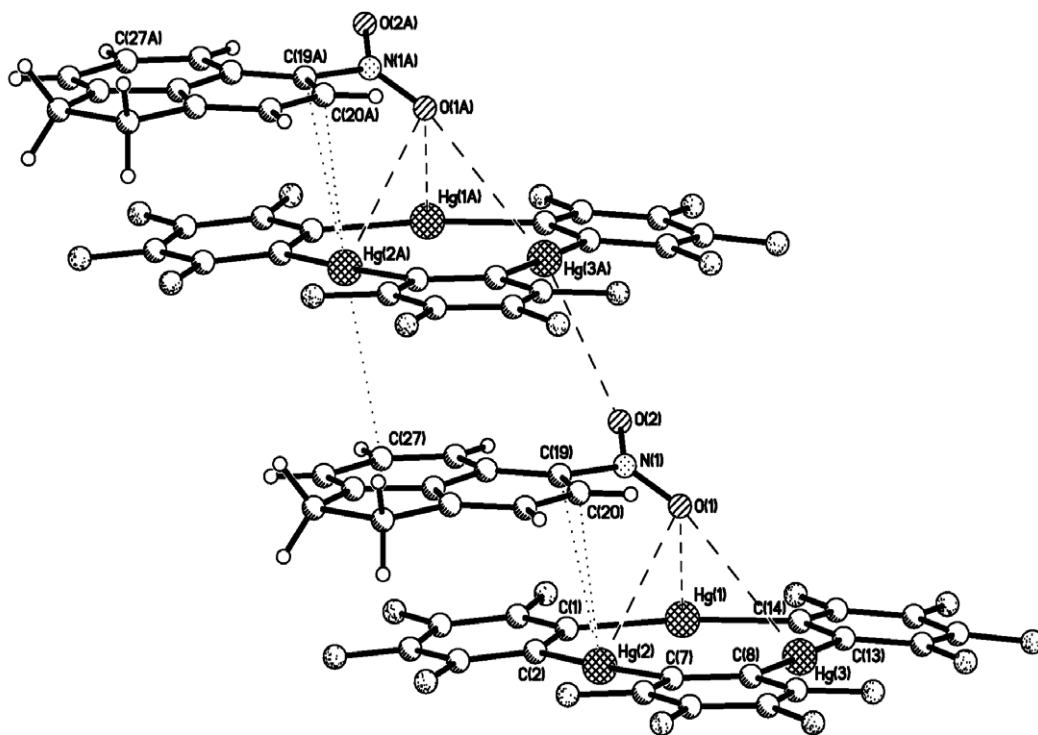

Fig. 5. View of a fragment of a polydecker sandwich structure of complex **4** in the crystal. The shortest intramolecular C···C contacts between the carbon atoms of the nitroarene and the neighbouring macrocycles are omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (°) in complex **4**

Hg(1)–O(1)	3.069(5)	N(1)–O(2)	1.193(7)
Hg(2)–O(1)	3.174(5)	C(19)–N(1)	1.546(10)
Hg(3)–O(1)	3.345(5)	Hg(1)–C(1)	2.071(6)
Hg(3A)–O(2)[a]	3.075(5)	Hg(1)–C(14)	2.075(6)
Hg(2)–C(19)	3.304(7)	Hg(2)–C(2)	2.083(6)
Hg(2)–C(20)	3.193(7)	Hg(2)–C(7)	2.082(6)
Hg(2A)–C(27)[a]	3.319(8)	Hg(3)–C(8)	2.066(6)
N(1)–O(1)	1.220(7)	Hg(3)–C(13)	2.071(6)
C(1)–Hg(1)–C(14)	172.9(2)	O(1)–N(1)–O(2)	125.7(6)
C(7)–Hg(2)–C(2)	175.6(2)	O(1)–N(1)–C(19)	112.5(6)
C(8)–Hg(3)–C(13)	177.6(2)	O(2)–N(1)–C(19)	121.8(6)

[a] Symmetry transformation $1 + x$, y, z was used to generate equivalent atoms.

centres of **1** and the carbon atoms of the nitroarene molecules (Hg(2)–C(20) 3.193(7) Å, Hg(2)–C(19) 3.304(7) Å, Hg(2A)–C(27) 3.319(8) Å) as well as shortened C–C contacts (3.280(9)–3.539(10) Å) between the carbon atoms of the nitroarene and the macrocycle. The mutual orientation of the macrocycles in **4** is close to an eclipsed conformation. The projections of the centroids of the neighbouring macrocycles onto the plane parallel to these cycles are shifted with respect to one another by 5.44 Å, thus leading to the ladder-like structure of **4**.

The structure of complex **6** is shown in Fig. 6. Selected bond lengths and angles for **6** are listed in Table 4. Unlike **2–5**, complex **6** contains three coordinated molecules of a nitro compound, two of which are located on one side of the metallacycle plane while the third nitroarene molecule is disposed on its other side. The pyrene rings of all three 1-nitropyrene ligands in **6** are practically parallel to the mean plane of the central nine-membered cycle of **1** (the corresponding interplane angles are in the range of 3–4°) but the oxygen atoms of the nitro groups are again deviated from the aromatic ring planes. The greatest deviation

is observed for the O(5) and O(6) atoms (the corresponding dihedral angle is 34.3°). In the case of the O(1) and O(2) atoms and the O(3) and O(4) atoms, these deviations are 19.9° and 23.9°, respectively. In contrast to **2–4**, each molecule of the nitroarene in complex **6** is bonded to **1** by a single oxygen atom which is coordinated only to one Hg centre (Hg(2) or Hg(3)). The shortest Hg–O distances are formed by the O(1) and O(3) atoms which interact with the Hg(2) and Hg(3) centres, respectively (Hg(2)–O(1) 2.862(6) Å, Hg(3)–O(3) 2.897(7) Å). The oxygen atom (O(6)) of the third nitropyrene ligand forms much longer Hg–O contact (Hg(3)–O(6) 3.568(11) Å) which do, however, remains slightly shorter than the corresponding van der Waals distance. An additional contribution to the bonding of this nitropyrene ligand to the macrocycle is made, apparently, by shortened Hg–C contacts between the Hg(1) and Hg(3) centres of **1** and the carbon atoms of the aromatic pyrene ring (Hg(1)–C(57) 3.264(8) Å, Hg(1)–C(54) 3.382(9) Å, Hg(3)–C(51) 3.372(9) Å, Hg(3)–C(56) 3.507(9) Å) as well as by shortened C–C contacts (3.301(10)–3.520(11) Å) between the aromatic pyrene ring and the adjacent C_6F_4 fragment of the macrocycle. The ability of **1** to give complexes with aromatic hydrocarbons (including unsubstituted pyrene) has previously been established by Gabbaï et al. [12]. These 1:1 complexes have polydecker sandwich structures in the solid state. In the case of the pyrene complex, the shortest Hg–C distances between the pyrene carbon atoms and the Hg sites of **1** range from 3.353(16) to 3.553(17) Å [12].

In the crystal, molecules of **6** are associated to form a complex three-dimensional structure. In this crystal structure, one may distinguish extended stacks wherein each two nearest macrocycle moieties are separated by three nitropyrene units belonging to three different molecules of the adduct. The bonding of the nitropyrene fragments in the stack to one another is accomplished due to aromatic stacking inter-
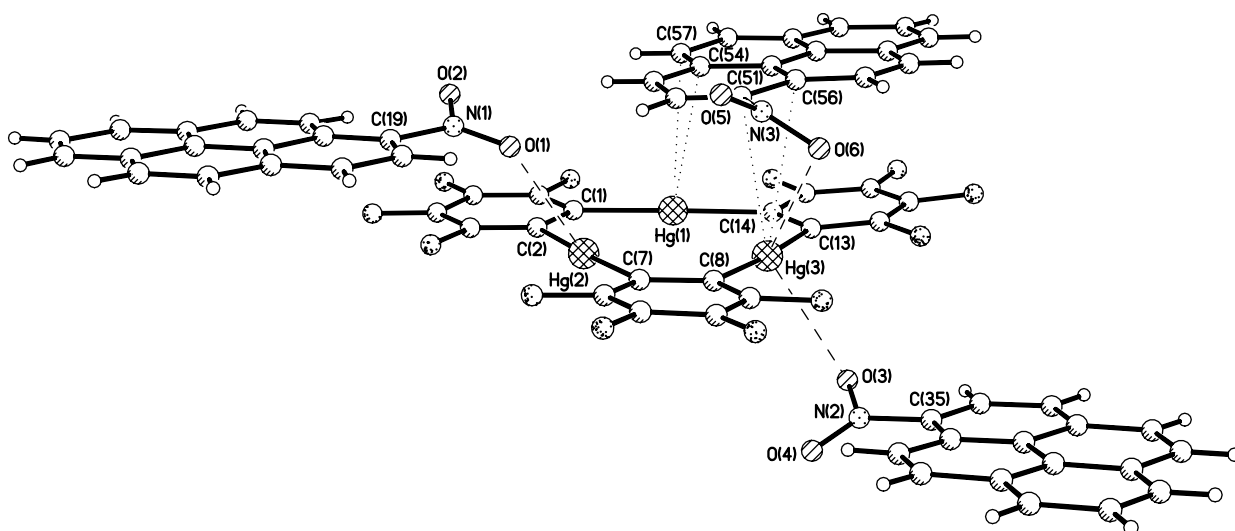

Fig. 6. Molecular structure of complex **6** in the crystal. The shortest intramolecular C···C contacts between the carbon atoms of the nitroarene and the neighbouring macrocycles are omitted for clarity.

Table 4
Selected bond lengths (Å) and angles (°) in complex **6**

Hg(2)–O(1)	2.862(6)	N(2)–O(4)	1.208(10)
Hg(3)–O(3)	2.897(7)	C(35)–N(2)	1.435(11)
Hg(3)–O(6)	3.568(11)	N(3)–O(5)	1.255(13)
Hg(1)–C(57)	3.264(8)	N(3)–O(6)	1.301(13)
Hg(1)–C(54)	3.382(9)	C(51)–N(3)	1.351(13)
Hg(3)–C(51)	3.372(9)	Hg(1)–C(1)	2.054(7)
Hg(3)–C(56)	3.507(9)	Hg(1)–C(14)	2.059(7)
N(1)–O(1)	1.239(8)	Hg(2)–C(2)	2.072(7)
N(1)–O(2)	1.223(8)	Hg(2)–C(7)	2.064(7)
C(19)–N(1)	1.461(9)	Hg(3)–C(8)	2.064(7)
N(2)–O(3)	1.289(10)	Hg(3)–C(13)	2.049(6)
C(1)–Hg(1)–C(14)	175.8(3)	O(3)–N(2)–O(4)	120.1(8)
C(2)–Hg(2)–C(7)	176.1(3)	O(4)–N(2)–C(35)	124.2(8)
C(8)–Hg(3)–C(13)	175.3(3)	O(3)–N(2)–C(35)	115.7(8)
O(1)–N(1)–O(2)	122.7(7)	O(5)–N(3)–O(6)	118.3(12)
O(2)–N(1)–C(19)	120.4(7)	O(5)–N(3)–C(51)	119.2(11)
O(1)–N(1)–C(19)	116.8(6)	O(6)–N(3)–C(51)	122.2(11)

actions (the shortest intermolecular C⋯C distances are in the range of 3.367(10)–3.479(11) Å, the distances between the planes of the adjacent pyrene rings are 3.44 and 3.55 Å) whereas the macrocycle and pyrene units are linked with each other due to shortened Hg⋯C (3.297(7)–3.431(7) Å) and C⋯C (3.382(11)–3.536(11) Å) contacts.

The geometry of the macrocycle does not change essentially upon its complexation with the above nitro compounds. The C–Hg–C bond angles in **2**–**4** and **6**, as in free **1**, are close to 180°. The Hg–C bond lengths are unexceptional and span the range of 2.049(6)–2.083(6) Å.

Returning now to the kinetics of the phase transfer acenaphthene nitration with dilute nitric acid in the presence of sodium nitrite as an initiator, sodium chloride as a promoter and macrocycle **1** as a catalyst [3e] (see Section 1), we note that the synthesized **4** is indeed better soluble in benzene than the starting **1**, particularly when an excess of 5-nitroacenaphthene is present in C_6H_6. Still further increase in the solubility of **4** and **1** in benzene is achieved on the combined use of 5-nitroacenaphthene and an aqueous solution of sodium chloride (see Section 4). These data suggest that the above-mentioned disappearance of the induction period in the phase transfer acenaphthene nitration (which was observed on the addition of nitroacenaphthenes to the benzene phase before the reaction [3e]) is due apparently to an enhancement in the solubility of both macrocycle **1** and its chloride complex in C_6H_6.

3. Conclusion

Macrocycle **1** readily binds various nitro compounds such as nitromethane, nitrobenzene, 5-nitroacenaphthene and 1-nitropyrene to afford complexes whose structures are strongly dependent on the nature of the starting nitro derivative. In 1:1 complex **2**, the nitromethane ligand behaves as a bidentate Lewis base, one oxygen atom of which interacts with three mercury centres (forming a pyramidal fragment) whereas the other is bonded to a single Hg atom. By contrast,

the nitrobenzene ligand in 1:1 complex **3** is bound by one of its oxygen atoms to only two Hg centres whereas the other oxygen atom coordinates again with a single Hg site. Quite different structure is realized in the case of the nitro-acenaphthene 1:1 complex **4** representing a polydecker sandwich in the crystal. In this adduct too, the NO_2 functionality of each nitroarene moiety acts as a bidentate Lewis base forming three Hg–O bonds with one of the adjacent macro-cycles and a single Hg–O bond with the other. Finally, in the 1:3 complex of **1** with 1-nitropyrene, the NO_2 group in all three nitroarene ligands behaves as a monodentate Lewis base and is coordinated only to one Lewis acidic Hg site of **1**. Note, in the previously described 1:3 complexes of **1** with DMSO [13], ethyl acetate [2a,2c,13] and acetone [2d], two of three Lewis basic species are cooperatively coordinated by all mercury centres of **1**, forming the corresponding bipyramidal fragment. A characteristic structural feature of complexes **4** and **6** is also the mutually parallel arrangement of **1** and the aromatic rings of the nitroarene units as well as the presence of shortened Hg–C contacts between the Hg sites of **1** and the carbon atoms of the nitro derivative. In addition, in the structures of **4** and **6** shortened C–C contacts between the carbon atoms of the coordinated nitroarene and **1** are observed.

4. Experimental

The starting macrocycle **1** was synthesized by the method described in [4a]. Commercial nitromethane and nitrobenzene were distilled prior to use, 1-nitropyrene was purified by sublimation in vacuum with subsequent recrystallization from EtOH–PhH mixture, commercial 5-nitroacenaphthene was used without additional purification. The IR spectra were recorded as Nujol mulls on a Nicolet Magna-IR 750 Series II Fourier spectrometer. The [199]Hg NMR spectra were recorded on a Bruker WP-200 SY instrument using Ph_2Hg in pyridine as an external standard.

4.1. Synthesis of complex 2

Compound **1** (0.1047 g, 0.1 mmol) was dissolved in 5 ml of boiling nitromethane and the resulting solution was cooled to room temperature; shortly, colourless crystals of complex **2** began to precipitate from the solution. Then, the reaction mixture was allowed to slowly evaporate to 0.5 ml at 20 °C. After 1 day, the precipitated fine colourless crystals of **2** were filtered off, washed with Et_2O (2 × 1 ml) and dried for 3 h at 20 °C in vacuum. The yield of **2** was 0.0809 g (73%). Anal. Calc. for $C_{19}H_3F_{12}Hg_3NO_2$: C, 20.62; H, 0.27; F, 20.59. Found: C, 20.38; H, 0.23; F, 19.83%.

4.2. Synthesis of complex 3

Compound **1** (0.1045 g, 0.1 mmol) was dissolved under heating (100–120 °C) in 1 ml of nitrobenzene and the resulting solution, after evaporation to 0.5 ml, was allowed

to stand at room temperature in a closed system. After 1 day, the precipitated colourless crystals of complex **3** were filtered off, washed with CH_2Cl_2 (2×0.5 ml) and dried for 3 h at 20 °C in vacuum. The yield of **3** was 0.0568 g (49%). Anal. Calc. for $C_{24}H_5F_{12}NO_2Hg_3$ (%): C, 24.64; H, 0.43; F, 19.50. Found: C, 24.54; H, 0.34; F, 19.73%.

4.3. Synthesis of complex 4

To a solution of **1** (0.1043 g, 0.1 mmol) in CH_2Cl_2 (15 ml) was added at room temperature a solution 5-nitro-acenaphthene (0.0203 g, 0.1 mmol) in CH_2Cl_2 (3 ml) and the resulting mixture was allowed to slowly evaporate for 2 days to 0.5 ml at 20 °C. Then, the precipitated orange-yellow fine-crystalline complex **4** was filtered off, washed with ether (2×1 ml) and dried for 3 h at 20 °C in vacuum. The yield of **4** was 0.0817 g (66%). Anal. Calc. for $C_{30}H_9F_{12}Hg_3NO_2$ (%): C, 28.94; H, 0.73; F, 18.31. Found: C, 28.92; H, 0.90; F, 17.95%.

4.4. Synthesis of complex 5

To a solution of **1** (0.1049 g, 0.1 mmol) in CH_2Cl_2 (15 ml) was added at room temperature a solution of 1-nitropyrene (0.0246 g, 0.1 mmol) in CH_2Cl_2 (3 ml). Within 5 min, yellow flakes of complex **5** began to precipitate. The subsequent slow evaporation of the reaction mixture to 2 ml at 20 °C for 5 days gave the fine-crystalline yellow powder of **5** which was filtered off, washed with CH_2Cl_2

(2×0.5 ml) and dried for 3 h at 20 °C in vacuum. The yield of **5** was 0.1059 g (82%). Anal. Calc. for $C_{34}H_9F_{12}Hg_3NO_2$: C, 31.58; H, 0.70; F, 17.63. Found: C, 31.45; H, 0.64; F, 17.66%.

4.5. Synthesis of complex 6

To a solution of 1-nitropyrene (0.0738 g, 0.3 mmol) in THF (3 ml) was added at room temperature a solution of **1** (0.1047 g, 0.1 mmol) in methanol (3 ml) and the reaction mixture was allowed to slowly evaporate to 0.5 ml at 20 °C. After 2 days, the precipitated yellow-orange crystals of complex **6** were filtered off, washed with Et_2O (3×1 ml) and dried for 4 h at 20 °C in vacuum. The yield of **6** was 0.1629 g (91%). Anal. Calc. for $C_{66}H_{27}F_{12}Hg_3N_3O_6$: C, 44.32; H, 1.51; F, 12.76. Found: C, 44.07; H, 1.67; F, 12.91%.

4.6. Experiments on the solubilization of 4 and 1 in benzene

An amount of 25 mg of complex **4** was stirred with 9 ml of a benzene solution of 5-nitroacenaphthene (0.25 g) at room temperature. In the course of stirring, approximately half the taken quantity of **4** dissolved in C_6H_6. Then, the resulting mixture was stirred with 4.5 ml of an aqueous solution of sodium chloride ([Cl^-] = 0.50 M), which led to a complete dissolution of the rest of the undissolved **4**. In the other experiment, a suspension of 21 mg of **1** in 9 ml of benzene, containing 0.25 g of 5-nitroacenaphthene,

Table 5
Crystal data, data collection and structure refinement parameters for **2**, **3**, **4** and **6**

Compound	2	3	4	6
Formula	$C_{19}H_3F_{12}Hg_3NO_2$	$C_{24}H_5F_{12}Hg_3NO_2$	$C_{30}H_9F_{12}Hg_3NO_2$	$C_{66}H_{27}F_{12}Hg_3N_3O_6$
Molecular weight	1106.99	1169.06	1245.15	1787.68
Crystal colour, habit	Colourless, plate	Colourless, prism	Orange, prism	Yellow, prism
Crystal size (mm^3)	$0.25 \times 0.20 \times 0.05$	$0.25 \times 0.20 \times 0.10$	$0.22 \times 0.08 \times 0.08$	$0.22 \times 0.15 \times 0.10$
Temperature (K)	120(2)	200(2)	120(2)	120(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/m$	$C2/c$	$P2_1/n$	$P\bar{1}$
a (Å)	6.7579(7)	20.390(3)	8.2949(5)	9.2798(5)
b (Å)	16.017(2)	17.289(3)	20.168(1)	15.2823(8)
c (Å)	9.751(1)	15.948(3)	17.099(1)	20.013(1)
α (°)	90	90	90	68.255(1)
β (°)	99.235(2)	119.454(3)	100.088(1)	86.166(1)
γ (°)	90	90	90	78.488(1)
V ($Å^3$)	1041.7(2)	4895(2)	2816.3(3)	2583.1(2)
Z	2	8	4	2
ρ_{calc} (g cm^{-3})	3.529	3.172	2.937	2.298
$2\theta_{max}$ (°)	58	60	58	60
μ (Mo $K\alpha$) (cm^{-1})	221.79	188.89	164.26	90.01
Minimum/maximum transmission factors	0.072/0.481	0.033/0.099	0.107/0.357	0.169/0.358
Number of collected reflections	10060	29052	30999	30698
Number of unique reflections (R_{int})	2795 (0.0411)	7126 (0.0477)	7480 (0.0522)	14843 (0.0438)
Number of observed reflections ($I > 2\sigma(I)$)	2447	5066	5502	10428
Number of parameters	175	379	433	811
R_1 (on F for observed reflections)[a]	0.0416	0.0374	0.0290	0.0461
wR_2 (on F^2 for all reflections)[b]	0.1008	0.0936	0.0592	0.1107

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

was stirred with 4.5 ml of a 0.50 M aqueous solution of NaCl at 20 °C. As a result, all the quantity of **1** dissolved in the organic layer. Under the same conditions but in the absence of 5-nitroacenaphthene, the major part of **1** remained undissolved in benzene.

4.7. X-ray diffraction study

Crystals of complex **2** for the X-ray diffraction study were obtained as described above but were not dried in vacuum. Crystals of complexes **3**, **4** and **6** were grown by slow evaporation of their solutions in CH_2Cl_2 (**3** and **4**) or in a EtOH–THF (2:3) mixture (**6**) and were not dried in vacuum as well. Details of crystal data, data collection and structure refinement parameters for **2–4** and **6** are given in Table 5. Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART 1000 CCD diffractometer (graphite monochromated Mo Kα radiation, $\lambda = 0.71073$ Å, ω-scans). Semi-empirical method SADABS [14] was applied for absorption correction. The structures were solved by direct methods and refined by the full-matrix least-squares technique against F^2 with the anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and included in the structure factors calculation in the riding motion approximation. Data reduction and further calculations were performed using SAINT [15] and SHELXTL-97 [16] program packages.

Acknowledgements

Appendix A. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre. CCDC 610041, 610042, 610043 and 610044 contain the supplementary crystallographic data for **2**, **3**, **4** and **6**. 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 doi:10.1016/j.jorganchem.2006.10.048.

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