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# Coordination chemistry of mercury-containing anticrowns. Complexation of nitrate and sulfate anions with the three-mercury anticrown $(o-C_6F_4Hg)_3$ and the influence of the nature of a countercation on the structure of the resulting nitrate complexes

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Dedicated to Professor Vladimir Bregadze on the occasion of his 75th birthday.

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# ABSTRACT

The interaction of the three-mercury anticrown  $(o-C_6F_4Hg)_3$  (1) with [PPN]NO<sub>3</sub> and [PPh<sub>4</sub>]NO<sub>3</sub> in an ethanol solution yields nitrate complexes,  $[PPN]{[(o-C_6F_4Hg)_3]_2(NO_3)}$  (2) and  $[PPh_4]{[(o-C_6F_4Hg)_3]_2(NO_3)}$  $C_{6}F_{4}Hg_{3}(NO_{3})$  (3), respectively, having double-decker sandwich structures. In both adducts, the nitrate anion behaves as a tridentate ligand and is coordinated through the oxygen atoms with the Hg sites of each anticrown unit in an  $\eta^3$ :  $\eta^1$  fashion. However, whereas complex **3** constitutes a bent sandwich in the crystal, the planes of the anticrown molecules in complex 2 are parallel to each other. The reaction of 1 with [PhNMe<sub>3</sub>]<sub>2</sub>SO<sub>4</sub> results in the formation of a sulfate complex, [PhNMe<sub>3</sub>]<sub>2</sub>{[ $(o-C_6F_4Hg)_3$ ]<sub>2</sub>(SO<sub>4</sub>)} (4), the subsequent recrystallization of which from the acetone/ethanol mixture yields a solvate, 4 Me<sub>2</sub>CO-3EtOH, representing also a double-decker sandwich according to X-ray crystallography. The sulfate anion in this sandwich is a tetradentate ligand and is bound to each anticrown species by two oxygen atoms in an  $\eta^3$ : $\eta^1$  fashion as well. Like **3**, complex **4**·Me<sub>2</sub>CO·3EtOH has a bent sandwich geometry. The complex is characterized also by the presence of H-bonds between two oxygen atoms of the coordinated sulfate anion and two ethanol molecules. The synthesized sandwich compounds 2, 3 and 4. Me<sub>2</sub>CO-3EtOH are the novel structural type of complexes of an anticrown with nitrate and sulfate anions as well as the first examples of structurally characterized complexes of 1 with oxygen-containing anions.

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# 1. Introduction

One of the promising approaches to the development of highly efficient and selective anion receptors is based on the use of macrocyclic multidentate Lewis acids or anticrowns [1] for this purpose. Over last two decades, the coordination and catalytic chemistry of these novel reagents representing charge-reversed analogs of crown ethers and related species has attracted considerable attention (see reviews [2–8] and recent papers cited in Refs. [9–22]). Among presently known anticrowns, the most studied is cyclic trimeric perfluoro-o-phenylenemercury ( $o-C_6F_4Hg$ )<sub>3</sub> (1) containing three Hg atoms in a planar nine-membered ring [23]. This remarkable compound was synthesized in 1968 by Sartory and

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Golloch [23a] but its ability to function as an anticrown was demonstrated for the first time in 1991 in our laboratory [24,25].



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Macrocycle **1** exhibits an extremely high affinity toward various anions and neutral Lewis bases [2,4-6,9-22] which is due to a strong electron-withdrawing effect of the fluorine substituents as well as ready steric accessibility of the Hg atoms. Particularly important is the capacity of **1** to bind Lewis basic species cooperatively by all Lewis acidic centres of the cycle which increases sharply the stability of the resulting complexes.

To date, complexes of 1 with bromide [24], iodide [25], thiocyanate [26], closo- $[B_{10}H_{10}]^2$  [27], closo- $[B_{12}H_{12}]^2$  [27], closo- $[B_{12}H_{11}SCN]^2$  [28], [Fe(CN)<sub>6</sub>]<sup>3</sup> [29], [Fe(CN)<sub>5</sub>(NO)]<sup>2</sup> [29] and [H<sub>3</sub>BCN]<sup>-</sup> [13] anions were prepared and structurally characterized. There are also spectroscopic data on the complexation of 1 in THF with borohydride, [p- $O_2NC_6H_4S$ <sup>-</sup> and  $[p-O_2NC_6H_4O]^-$  anions [4,30]. According to X-ray crystallography, the 1:1 complexes of **1** with bromide, iodide and thiocyanate anions form in the crystal infinite chains representing bent polydecker sandwiches [24-26]. The interaction of the abovementioned polyhedral anionic boranes as well as  $[Fe(CN)_6]^{3-}$  with a twofold excess of 1 yields the corresponding bent double-decker sandwiches {[(o-C<sub>6</sub>F<sub>4</sub>Hg)<sub>3</sub>]<sub>2</sub>(B<sub>10</sub>H<sub>10</sub>)}<sup>2-</sup>, {[(o-C<sub>6</sub>F<sub>4</sub>Hg)<sub>3</sub>]<sub>2</sub>(B<sub>12</sub>H<sub>12</sub>)]<sup>2-</sup>, {[(o-C<sub>6</sub>F<sub>4</sub>Hg)<sub>3</sub>]<sub>2</sub>(B<sub>12</sub>H<sub>12</sub>)]<sup>2-</sup>, {[(o-C<sub>6</sub>F<sub>4</sub>Hg)<sub>3</sub>]<sub>2</sub>(B<sub>12</sub>H<sub>11</sub>SCN)]<sup>2-</sup> and {[(o-C<sub>6</sub>F<sub>4</sub>Hg)<sub>3</sub>]<sub>2</sub>[Fe(CN)<sub>6</sub>]}<sup>3-</sup> [27-29]. At the same time, the double-decker sandwich complexes {[(o- $C_{6}F_{4}Hg_{3}_{2}[Fe(CN)_{5}(NO)]^{2-}$  [29] and {[(o- $C_{6}F_{4}Hg_{3}_{3}_{2}(H_{3}BCN)^{-}$  [13], isolated from the reactions of **1** with  $[Fe(CN)_5(NO)]^{2-}$  and  $[H_3BCN]^{-}$ , are characterized by a parallel arrangement of the anticrown rings. In all of the above double-decker sandwiches, the BH or/and CN groups of the anionic guest are involved in the coordination with the Hg atoms of the anticrown moieties and in the case of {[(o- $C_{6}F_{4}Hg_{3}]_{2}(B_{12}H_{11}SCN)\}^{2-}$  the sulfur atom of the SCN substituent takes part in the bonding along with the BH groups.

In the present article, data on the complexation of **1** with nitrate and sulfate anions are reported. The results of this study demonstrate for the first time the influence of the nature of a countercation upon the structure of complexes of an anticrown with anionic species.

#### 2. Results and discussion

The interaction of macrocycle **1** with [PPN]NO<sub>3</sub>·H<sub>2</sub>O (where PPN is (Ph<sub>3</sub>P)<sub>2</sub>N<sup>+</sup>) in an ethanol solution at room temperature (**1**:NO<sub>3</sub><sup>-</sup> = 2:1) leads to precipitation of a colorless, fine crystalline solid which was identified as a nitrate complex [PPN]{[( $o-C_6F_4Hg)_3$ ]<sub>2</sub>(NO<sub>3</sub>)} (**2**), containing two anticrown species per one nitrate anion, on the basis of elemental analysis. The complex was obtained in 61% yield. The room-temperature <sup>199</sup>Hg NMR spectrum of **2** in THF ([**2**]<sub>0</sub> = 4 × 10<sup>-2</sup> M) exhibits a downfield <sup>199</sup>Hg shift of 12.0 ppm relative to that of neat **1**, thus suggesting the presence of anticrown molecules coordinated with nitrate anions in the solution.

In the crystal, complex 2 occupies a special position on the inversion centre which results in disordering the nitrate anion over two positions. As seen from Fig. 1, the complex has a double-decker sandwich structure. The nitrate anion in 2 is disposed between the mutually parallel planes of two anticrown units and behaves as a tridentate ligand, forming two types of coordination bonds with the molecules of 1. One type is the cooperative bonding of the oxygen atoms O(1) and O(2) of the nitrate anion by all three Hg sites of the neighboring molecule of the anticrown. The Hg–O distances in these  $\eta^3$  coordination fragments of the complex range from 2.676(6) to 3.260(9) Å (av. 2.92 Å; see Table 1) and they are all within the sum of the van der Waals radii of mercury (1.73–2.00 Å [31a,b], 2.1 Å [31c]) and oxygen (1.54 Å [31d]) atoms. Another type of the bonding is realized with the participation of the oxygen atom O(3) which forms a relatively short Hg–O contact (3.137(8) Å) with one of the molecules of the anticrown and a considerably longer Hg–O contact (3.543(8) Å) with the other molecule of **1**.



**Fig. 1.** Molecular structure of complex **2** in the crystal. Only one of two positions of the disordered nitrate anion is depicted; the hydrogen atoms of the PPN cation are omitted for clarity.

The coordinated nitrate ion in **2** retains its planar trigonal geometry and the lengths of the N–O bonds (1.22(2), 1.25(4) and 1.25(3) Å) are changed only slightly, if any, as a result of the complexation with **1** (the N–O distances in free NO<sub>3</sub><sup>-</sup> ion are 1.239 Å [32]). The plane of the nitrate anion in **2** is practically perpendicular to the mean planes of the central nine-membered rings of the macrocycles (the corresponding interplane angle is 88°). The mutual orientation of the mercury macrocycles in the complex corresponds to a staggered conformation and the projections of their centroids onto the plane parallel to these cycles are shifted relative to each other only by 0.35 Å. The [PPN]<sup>+</sup> countercation in **2** as in the majority of other salts of this cationic species [33] has a bent geometry (the P(1)–N(2)–P(2) bond angle is 157.2(4)°).

In the crystal structure of complex **2**, the {[ $(o-C_6F_4Hg)_3$ ]<sub>2</sub>(NO<sub>3</sub>)}<sup>-</sup> anions form layers which are parallel to *ab* crystal plane. The formation of these layers is due mainly to stacking interactions between the perfluorinated *o*-phenylene rings (the corresponding intermolecular C···C distances are 3.291(5)–3.326(6) Å) as well as shortened (as compared to the sum of the van der Waals radii) intermolecular Hg···Hg (3.8446(3) Å) and Hg···C (3.437(4)–3.655(4) Å) contacts between the neighboring anionic units. The anionic layers in the crystal of **2** alternate with the corresponding cationic [PPN]<sup>+</sup> layers which are parallel to the same crystal plane. The crystal structure of complex **2** contains also shortened C–F···H contacts (2.46–2.50 Å) between the anticrown moieties and the [PPN]<sup>+</sup> countercations.

The nitrate complex of analogous composition,  $[PPh_4]\{[(o-C_6F_4Hg)_3]_2(NO_3)\}$  (**3**), was isolated as colorless crystals in 66% yield from the interaction of **1** with  $[PPh_4]NO_3$  in ethanol at

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

<b>.</b>		*	
Hg(1)-O(1)	2.676(6)	Hg(3)-O(3)	3.543(8)
Hg(2)-O(1)	2.871(7)	$Hg(1A)-O(3)^{a}$	3.137(8)
Hg(3)-O(1)	3.260(9)	N(1)-O(1)	1.25(3)
$Hg(1A) - O(2)^{a}$	3.163(8)	N(1)-O(2)	1.25(4)
$Hg(2A) - O(2)^{a}$	2.833(6)	N(1)-O(3)	1.22(2)
$Hg(3A) - O(2)^{a}$	2.708(6)		
O(1)-N(1)-O(2)	120.7(13)	O(2) - N(1) - O(3)	119(2)
O(1)-N(1)-O(3)	120(3)		

<sup>a</sup> Symmetry transformation -x, -y, -z+1 was used to generate equivalent atoms.



Fig. 2. Molecular structure of complex 3 in the crystal. The hydrogen atoms of the tetraphenylphosphonium cation are omitted for clarity.

room temperature ( $1:NO_3^- = 2:1$ ). However, it turned out unexpectedly that this complex differs in its structure from **2** and has a bent double-decker sandwich geometry.

The structure of **3** is depicted in Fig. 2. Selected bond lengths and angles for **3** are listed in Table 2. As in **2**, the nitrate anion in complex **3** is located between the planes of two anticrown species but these planes in **3**, in contrast to those in **2**, are not parallel to one another (the dihedral angle between the mean planes of the central 9-membered rings of the macrocycles is  $34.2^{\circ}$ ). Interestingly, despite this difference, the nitrate anion in complex **3** behaves again as a tridentate ligand and, as in **2**, is bonded to each anticrown unit in an  $\eta^3:\eta^1$  fashion. The Hg–O distances in the  $\eta^3$  coordination fragments of **3** span the range 2.688(3)–3.276(3) Å (av. 2.93 Å) and are comparable with the corresponding distances in **2**. An additional contribution to the bonding is made by the oxygen atom O(3) which coordinates to a single Hg atom of each anticrown molecule. The Hg–O distances in these  $\eta^1$  coordination fragments of the complex (Hg(3)–O(3) 2.885(3) Å, Hg(6)–O(3) 2.723(3) Å) are considerably shorter than those in **2**.

The geometry of the nitrate anion in complex **3**, as in **2**, is close to that of uncoordinated  $NO_3^-$  ion. The room-temperature <sup>199</sup>Hg NMR spectrum of **3** in THF ([**3**]<sub>0</sub> = 4 × 10<sup>-2</sup> M) is characterized by a downfield <sup>199</sup>Hg shift of 12.2 ppm relative to that of free **1**. The closeness of the <sup>199</sup>Hg shifts for **2** (see above) and **3** may indicate on the identical structure of these complexes in the solution.

Previously, Hawthorne and co-workers described two *bis*-nitrate complexes of *o*-carboranyl-mercury anticrown (*o*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>Hg)<sub>4</sub> which contains four Hg atoms in a 12-membered cycle [34]. In one of these complexes, {[(*o*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>Hg)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>)<sup>2-</sup>, both nitrates are bonded to the anticrown molecule in an unusual tridentate, face-on fashion, whereas in the other complex, {[(*o*-C<sub>2</sub>B<sub>10</sub>H<sub>10</sub>Hg)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)]<sup>2-</sup>, the nitrate species behave as monodentate ligands and coordinate with the macrocycle in an  $\eta^4$  and  $\eta^2$  fashion respectively.

Table 2	
Selected bond lengths (Å) and angles (°) in complex <b>3</b> .	

Hg(1) - O(1)	2.688(3)	Hg(3)-O(3)	2.885(3)
Hg(2)-O(1)	2.835(3)	Hg(6)–O(3)	2.723(3)
Hg(3)-O(1)	3.276(3)	N(1)-O(1)	1.254(4)
Hg(4)-O(2)	2.832(3)	N(1)-O(2)	1.245(4)
Hg(5)-O(2)	2.924(3)	N(1)-O(3)	1.248(5)
Hg(6)-O(2)	3.001(3)		
O(1)-N(1)-O(2)	120.3(4)	O(2)-N(1)-O(3)	120.5(3)
O(1)-N(1)-O(3)	119.2(4)		



**Fig. 3.** Molecular structure of complex  $4 \cdot Me_2CO \cdot 3EtOH$  in the crystal. The hydrogen atoms of the phenyltrimethylammonium cations as well as of the alkyl groups of the acetone and ethanol molecules are omitted for clarity.

Sulfate complexes of macrocycle **1** were obtained in 74–78% yield by the interaction of **1** with [PhNMe<sub>3</sub>]<sub>2</sub>SO<sub>4</sub>·3H<sub>2</sub>O and [PPh<sub>3</sub>Me]<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O at room temperature in CH<sub>2</sub>Cl<sub>2</sub> (**1**:SO<sub>4</sub><sup>2-</sup> = 2:1). The complexes have composition [PhNMe<sub>3</sub>]<sub>2</sub>{[( $o-C_6F_4Hg$ )<sub>3</sub>]<sub>2</sub>(SO<sub>4</sub>)} (**4**) and [PPh<sub>3</sub>NMe]<sub>2</sub>{[( $o-C_6F_4Hg$ )<sub>3</sub>]<sub>2</sub>(SO<sub>4</sub>)} (**5**) respectively, i.e. contain, as in the case of **2** and **3**, two anticrown hosts per one anionic guest. The room-temperature <sup>199</sup>Hg NMR spectrum of **5** in [D<sub>6</sub>]acetone ([**5**]<sub>0</sub> = 4 × 10<sup>-2</sup> M) shows a downfield <sup>199</sup>Hg shift of 52.0 ppm relative to that of neat **1**, thus indicating on the presence of the molecules of **1** coordinated with sulfate anions in the solution. Attempts to obtain a satisfactory <sup>199</sup>Hg NMR spectrum of **c** in organic solvents.

Recrystallization of complex **4** from the acetone/ethanol mixture (1:1) gave crystals suitable for the X-ray diffraction study. The crystals were not dried and contained one molecule of acetone and three ethanol molecules per one molecule of **4** according to X-ray crystallography. Unfortunately, good single crystals of complex **5** could not be grown despite numerous attempts.

Fig. 3 shows the structure of  $4 \cdot \text{Me}_2\text{CO} \cdot 3\text{EtOH}$ . Like **3**, complex  $4 \cdot \text{Me}_2\text{CO} \cdot 3\text{EtOH}$  represents a bent double-decker sandwich in the crystal (the dihedral angle between the mean planes of the central 9-membered rings of the macrocycles is  $43.0^{\circ}$ ). The sulfate anion in the complex behaves as a tetradentate ligand and coordinates with each anticrown moiety by two oxygen atoms in an  $\eta^3:\eta^1$  fashion. The Hg–O separations in the  $\eta^3$  coordination fragments of the adduct are in the range of 2.602(9)-2.702(9) Å (av. 2.65 Å; see Table 3) and are significantly shorter than the analogous Hg–O separations in complexes **2** (av. 2.92 Å) and **3** (av. 2.93 Å). The  $\eta^1$  coordination Hg–O bonds in  $4 \cdot \text{Me}_2\text{CO} \cdot 3\text{EtOH}$  are formed by the

Selected bond lengths (Å) and angles (°) in complex $4 \cdot Me_2CO \cdot 3EtOH$ .				
Hg(1)-O(1)	2.647(9)	S(1)-O(1)	1.468(9)	
Hg(2) - O(1)	2.661(10)	S(1)-O(2)	1.474(9)	
Hg(3)-O(1)	2.646(10)	S(1)-O(3)	1.455(10)	
Hg(4) - O(2)	2.602(9)	S(1)-O(4)	1.483(11)	
Hg(5) - O(2)	2.648(8)	O(1S)…O(3)	2.75(1)	
Hg(6)-O(2)	2.702(9)	O(2S)…O(4)	2.61(2)	
Hg(2)-O(3)	2.978(9)	O(3S)…O(2S)	2.87(3)	
Hg(6) - O(4)	2.948(10)			
O(1)-S(1)-O(2)	108.4(5)	O(2) - S(1) - O(3)	110.4(6)	
O(1)-S(1)-O(3)	110.2(6)	O(2) - S(1) - O(4)	108.6(6)	
O(1)-S(1)-O(4)	109.4(7)	O(3)-S(1)-O(4)	109.8(6)	

Table 3

oxygen atoms O(3) and O(4) which interact with the Hg(2) and Hg(6) atoms respectively. The corresponding Hg(2)–O(3) and Hg(6)–O(4) separations (2.978(9) and 2.948(10) Å) are considerably shorter than the analogous Hg–O separations in **2** (3.137(8) and 3.543(8) Å) but noticeably longer than those in **3** (2.885(3) and 2.723(3) Å).

The  $\eta^1$  coordinated oxygen atoms O(3) and O(4) of the sulfate anion in **4**·Me<sub>2</sub>CO·3EtOH are involved also in the formation of Hbonds with two ethanol molecules (O(1S)···O(3) 2.75(1) Å, O(2S)··· O(4) 2.61(2) Å). In its turn, one of these molecules forms H-bond with the third ethanol species in the complex (O(3S)···O(2S) 2.87(3) Å).

The coordinated sulfate anion retains its tetrahedral configuration and the S–O distances in the complex (1.455(10)–1.483(11) Å; av. 1.47 Å) are close to the length of the S–O bonds in free SO<sub>4</sub><sup>2–</sup> ion (1.472 Å [32]).

The only known complex of an anticrown with sulfate anion has been obtained for the five-mercury macrocycle  $[(CF_3)_2CHg]_5$  containing the Hg atoms in a planar ten-membered ring [4]. The sulfate anion in this 1:1 complex  $\{[(CF_3)_2CHg]_5(SO_4)\}^{2-}$  serves again as a tetradentate ligand but coordinates to the anticrown molecule in an  $\eta^5:\eta^2:\eta^1:\eta^1$  fashion. One more interesting feature of the complex is the arrangement of the  $\eta^5$  coordinated oxygen atom of the sulfate anion virtually in the plane of the ten-membered mercuracarbon ring.

In the crystal, the anionic parts of complexes 3 and 4. Me<sub>2</sub>CO. 3EtOH form extended stacks due to shortened (as compared to the sum of the van der Waals radii) intermolecular Hg. Hg. Hg. C and C. C contacts between the neighboring sandwich units of the adduct (3: Hg...Hg 3.5570(2) and 3.8250(2) Å, Hg...C 3.295(4)-3.712(4) Å, C···C 3.299(6)-3.517(6) Å; 4·Me<sub>2</sub>CO·3EtOH: Hg...Hg 3.754 (1) Å, Hg...C 3.40(1)-3.68(1) Å, C...C 3.35(2)-3.53(3) Å). The stacks are disposed along c crystal axis in the case of **3** and along b crystal axis in the case of  $4 \cdot Me_2CO \cdot 3EtOH$ . The distance between the mean planes of the central  $Hg_3C_6$  rings of the adjacent mercuramacrocycles in the stack is 3.412 Å in 3 and 3.51 Å in 4 · Me<sub>2</sub>CO · 3EtOH. The formation of similar stacks was earlier observed in the crystal structures of the double-decker sandwich complexes of 1 with  $closo-[B_{10}H_{10}]^{2-}$ ,  $closo-[B_{12}H_{12}]^{2-}$ , closo- $[B_{12}H_{11}SCN]^{2-}$ ,  $[Fe(CN)_6]^{3-}$  and  $[Fe(CN)_5(NO)]^{2-}$  anions [27–29] as well as with metallocenes [35,36] p-benzoquinone [37], [9] thiacrown-3[10] and [12]crown-4[15]. As in the case of 2, the anticrown units in the crystal structures of **3** and **4** · Me<sub>2</sub>CO · 3EtOH form also shortened C-F...H contacts (2.40-2.59 Å in 3, 2.41-2.58 Å in  $4 \cdot Me_2CO \cdot 3EtOH$ ) with the C–H bonds of the countercations.

The complexation of **1** with nitrate and sulfate anions does not affect essentially the geometry of the macrocycle. The Hg–C bond lengths in **2** (2.069(3)–2.080(4) Å), **3** (2.064(5)–2.085(4) Å) and **4**·Me<sub>2</sub>CO·3EtOH (2.04(2)–2.10(2) Å) are unexceptional. The C–Hg–C bond angles, as in free **1**, are close to  $180^{\circ}$  (175.3(2)– $175.9(2)^{\circ}$  in **2**, 174.5(2)– $176.8(2)^{\circ}$  in **3**, 172.6(7)– $175.5(6)^{\circ}$  in **4**·Me<sub>2</sub>CO·3EtOH).

#### 3. Conclusion

The results of our study demonstrate the ability of the threemercury anticrown **1** to bind nitrate and sulfate anions with the formation of double-decker sandwich complexes. In the case of nitrate anions, two complexes **2** and **3** differing from each other by the nature of a countercation were prepared and structurally characterized. The nitrate anion in these complexes is bonded to the molecules of **1** in a similar fashion but whereas complex **3** has a bent sandwich geometry in the crystal the planes of the anticrown units in **2** are parallel to one another. A more detailed analysis of the structures of **2** and **3** did not reveal any bonding contacts between the atoms of the cationic and anionic parts of the complexes, which would explain the above-mentioned difference in the geometry of the sandwich moieties. Therefore, one may conclude that the observed difference is the result of packing effects which are assisted by secondary character of the Hg–O coordination bonds in these supramolecular adducts.

In the case of sulfate anions, two complexes (**4** and **5**) distinguishing by the nature of a countercation were obtained as well however the X-ray diffraction study could be carried out only for complex **4** in a form of its solvate  $4 \cdot Me_2CO \cdot 3EtOH$ . The complex contains H-bonds between two oxygen atoms of the coordinated sulfate anion and two ethanol molecules and, like **3**, represents a bent sandwich.

A comparison of the synthesized complexes **2**, **3** and **4**·Me<sub>2</sub>CO·3EtOH shows that the shortest Hg–O distances (2.602(9)–2.702(9) Å; av. 2.65 Å) are realized here in the case of the  $\eta^3$  coordination fragments of **4**·Me<sub>2</sub>CO·3EtOH. These distances are considerably shorter than the Hg–O bond lengths in all presently known complexes of **1** with oxygenous Lewis bases (aldehydes and ketones, 2.810(12)–3.088(8) Å [37–39]; organic amides, 2.777(4)–3.024(5) Å [40–42]; ethyl acetate, 2.848(5)–2.975(5) Å [41]; HMPA, 2.824(4)–2.895(4) Å [41]; DMSO, 2.759(5)–3.120(5) Å [41]; THF, 2.853(3)–3.621(9) Å [14]; etc. [14,15,19]). The Hg(1)–O(1) and Hg(3A)–O(2) bonds in **2** (2.676(6) and 2.708(6) Å) and the Hg(1)–O(1) bond in **3** (2.688(3) Å) are also significantly shortened but the other Hg–O distances in these nitrate complexes are comparable on the whole with those in the above-mentioned complexes of **1** with oxygenous Lewis bases.

The synthesized sandwich compounds **2**, **3** and **4**  $\cdot$  Me<sub>2</sub>CO  $\cdot$  3EtOH are the novel structural type of complexes of nitrate and sulfate anions with an anticrown as well as the first examples of structurally characterized complexes of **1** with oxygen-containing anions.

#### 4. Experimental

The starting macrocycle **1** was prepared according to the published procedure [23a]. Commercial bis(triphenylphosphoranylidene)ammonium chloride [PPN]Cl (Aldrich; 97%), phenyltrimethylammonium iodide [PhNMe<sub>3</sub>]I (Chemapol Prague), tetraphenylphosphonium bromide [PPh<sub>4</sub>]Br (Chemapol Prague), tetraphenylmethylphosphonium iodide [PPh<sub>3</sub>Me]I (Chemapol Prague), anhydrous potassium nitrate, silver sulfate and silver nitrate were used without an additional purification. Solvents were purified by conventional methods and freshly distilled prior to use over calcium hydride (ethanol, acetone), P<sub>2</sub>O<sub>5</sub> (CH<sub>2</sub>Cl<sub>2</sub>), metallic sodium (*n*-hexane) or LiAlH<sub>4</sub>(Et<sub>2</sub>O) under Ar. The <sup>199</sup>Hg NMR spectra were recorded on a Bruker Av-600 instrument using a 0.2 M solution of Ph<sub>2</sub>Hg in pyridine ( $\delta = -791.1$  ppm [43]) as an external standard. The IR spectra of complexes were recorded as Nujol mulls on a Nicolet Magna-IR 750 Series II Fourier spectrometer.

#### 4.1. Synthesis of [PPN]NO<sub>3</sub>·H<sub>2</sub>O

To a solution of [PPN]Cl (0.287 g, 0.5 mmol) in a mixture of water (15 mL) and ethanol (2 mL) was added upon stirring at room temperature a solution of KNO<sub>3</sub> (0.051 g, 0.5 mmol) in water (2 mL). Immediately, a white powder of [PPN]NO<sub>3</sub>·H<sub>2</sub>O began to precipitate. Then, the reaction mixture was stirred for 1 h, the resulting [PPN]NO<sub>3</sub>·H<sub>2</sub>O was filtered off, washed with water (3 × 2 mL) and dried at 20 °C in vacuum for 5 h. Yield: 0.302 g (98%). Anal. Calcd. for C<sub>36</sub>H<sub>32</sub>N<sub>2</sub>O<sub>4</sub>P<sub>2</sub> (%): C, 69.90; H, 5.21; N, 4.53. Found: C, 70.03; H, 4.84; N, 4.31. IR ( $\nu_{OH}$ , cm<sup>-1</sup>): 3530 (br), 3462 (br).

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Crystal data, data collection and structure refinement parameters for **2**, **3** and **4**·Me<sub>2</sub>CO·3EtOH.

	2	3	$4 \cdot Me_2CO \cdot 3EtOH$
Formula	$C_{72}H_{30}F_{24}Hg_6N_2O_3P_2$	$C_{60}H_{20}F_{24}Hg_6NO_3P$	C <sub>63</sub> H <sub>52</sub> F <sub>24</sub> Hg <sub>6</sub> N <sub>2</sub> O <sub>8</sub> S
Molecular weight	2692.46	2493.28	2656.67
Crystal size (mm <sup>3</sup> )	$0.36 \times 0.31 \times 0.16$	0.27 imes 0.15 imes 0.15	$0.22\times0.07\times0.06$
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	PĪ	P21/c	P21/n
a (Å)	9.0108(4)	12.0036(3)	17.062(2)
b (Å)	10.6179(5)	26.3521(7)	17.549(2)
<i>c</i> (Å)	18.1790(9)	18.8943(5)	23.481(2)
α (°)	101.593(1)	90	90
$\beta$ (°)	101.252(1)	95.094(1)	91.015(2)
γ (°)	93.165(1)	90	90
$V(A^3)$	1663.0(1)	5953.0(3)	7030(1)
Ζ	1	4	4
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	2.689	2.782	2.510
Linear absorption ( $\mu$ ), mm <sup>-1</sup>	13.965	15.566	13.203
$T_{\min}/T_{\max}$	0.029/0.215	0.056/0.233	0.252/0.505
$2\theta_{\max}$ (°)	64	64	54
No. unique refl. ( <i>R</i> <sub>int</sub> )	11,488 (0.0403)	20,633 (0.0667)	15,224 (0.0935)
No. observed refl. $(I > 2\sigma(I))$	9413	16,130	9206
No. parameters	514	856	940
$R_1$ (on F for observed refl.) <sup>a</sup>	0.0265	0.0281	0.0550
wR <sub>2</sub> (on F <sup>2</sup> for all refl.) <sup>b</sup>	0.0525	0.0568	0.1293
GOOF	0.995	1.006	1.036

 ${}^{a} R_{1} = \Sigma ||F_{o}| - |F_{c}||/\Sigma |F_{o}|.$ 

<sup>b</sup>  $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}.$ 

## 4.2. Synthesis of [PPh<sub>4</sub>]NO<sub>3</sub>

To a solution of [PPh<sub>4</sub>]Br (0.42 g, 1.0 mmol) in a mixture of water (18 mL) and ethanol (2 mL) was added upon stirring at room temperature a solution of AgNO<sub>3</sub> (0.17 g, 1.0 mmol) in water (2 mL). Immediately, a yellowish powder of AgBr began to precipitate. The reaction mixture was stirred in darkness for 1 h, then it was centrifuged for 10 min at 5000 rpm and filtered off. The resulting colorless filtrate was concentrated to ~2 mL in vacuum and then kept overnight in refrigerator. The next day, the precipitated colorless crystals of [PPh<sub>4</sub>]NO<sub>3</sub> were filtered off, washed with cold water (4 × 0.5 mL) and dried at 20 °C in vacuum for 5 h. Yield: 0.33 g (82%). Anal. Calcd. for C<sub>24</sub>H<sub>20</sub>NO<sub>3</sub>P (%): C, 71.81; H, 5.02; N, 3.49; P, 7.72. Found: C, 71.96; H, 4.88; N, 3.46; P, 7.72.

The synthesis of [PPh<sub>4</sub>]NO<sub>3</sub> by combining hot solutions of ethanolic [PPh<sub>4</sub>]Br and aqueous AgNO<sub>3</sub> has been previously described very shortly in Ref. [44]. However elemental analysis data for the product obtained and its isolated yield are not reported in this article.

#### 4.3. Synthesis of [PPh<sub>3</sub>Me]<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O

To a solution of [PPh<sub>3</sub>Me]I (0.40 g, 1.0 mmol) in a mixture of water (15 mL) and ethanol (1.5 mL) was added upon stirring a suspension of Ag<sub>2</sub>SO<sub>4</sub> (0.15 g, 0.5 mmol) in water (3 mL). Immediately, a yellow powder of Agl began to precipitate. The reaction mixture was stirred for 2.5 h in darkness and filtered off. The colorless filtrate was evaporated in vacuum, the resulting resinous product was washed with acetone (3 × 5 mL) and kept under acetone in refrigerator overnight to give a white powder of [PPh<sub>3</sub>Me]<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O which was filtered off, washed with acetone (2 × 1 mL) and dried at 20 °C in vacuum for 3 h. Yield: 0.31 g (95%). Anal. Calcd. for C<sub>38</sub>H<sub>40</sub>O<sub>6</sub>P<sub>2</sub>S (%): C, 66.46; H, 5.87; P, 9.02. Found: C, 66.88; H, 5.93; P, 8.99. IR ( $\nu_{OH}$ , cm<sup>-1</sup>): 3412 (br), 3375 (br).

#### 4.4. Synthesis of [PhNMe<sub>3</sub>]<sub>2</sub>SO<sub>4</sub>·3H<sub>2</sub>O

To a suspension of  $Ag_2SO_4$  (0.313 g, 1.0 mmol) in 20 mL of water was added upon stirring a solution of [PhNMe<sub>3</sub>]I (0.526 g,

2.0 mmol) in 10 mL of water. Immediately, a yellow powder of AgI began to precipitate. The reaction mixture was stirred in darkness for 1 h and filtered off, the colorless filtrate was evaporated at 20 °C in vacuum and the resulting resinous product was dried at 70–80 °C in vacuum for 2 h to give [PhNMe<sub>3</sub>]<sub>2</sub>. SO<sub>4</sub>·3H<sub>2</sub>O as a colorless crystalline solid. Yield: 0.382 g (90%). Anal. Calcd. for C<sub>18</sub>H<sub>34</sub>N<sub>2</sub>O<sub>7</sub>S (%): C, 51.17; H, 8.11; N, 6.63. Found: C, 51.31; H, 8.18; N, 6.55. IR ( $\nu_{OH}$ , cm<sup>-1</sup>): 3370 (br). The synthesized compound is hygroscopic and should be kept in desiccator over NaOH or P<sub>2</sub>O<sub>5</sub>.

# 4.5. Synthesis of [PPN]{[(o-C<sub>6</sub>F<sub>4</sub>Hg)<sub>3</sub>]<sub>2</sub>(NO<sub>3</sub>)} (**2**)

To a solution of macrocycle **1** (0.1032 g, 0.1 mmol) in ethanol (8 mL) was added at room temperature a solution of [PPN] NO<sub>3</sub>·H<sub>2</sub>O (0.0303 g, 0.05 mmol) in ethanol (4 mL). Within 2 h, a colorless crystalline complex **2** began to precipitate. The next day, the reaction mixture was slowly concentrated for 6 h to 2 mL and the resulting **2** was filtered off, washed with ethanol ( $3 \times 0.5$  mL) and diethyl ether ( $3 \times 0.5$  mL) and dried at 20 °C in vacuum for 3.5 h. Yield: 0.0806 g (61%). Anal. Calcd. for C<sub>72</sub>H<sub>30</sub>F<sub>24</sub>Hg<sub>6</sub>N<sub>2</sub>O<sub>3</sub>P<sub>2</sub> (%): C, 32.12; H, 1.12; F, 16.93. Found: C, 32.48; H, 0.94; F, 16.87. Single crystals of **2** for the X-ray diffraction study were grown from the acetone/ethanol mixture (1:2) and were not dried in vacuum.

#### 4.6. Synthesis of $[PPh_4]{[(o-C_6F_4Hg)_3]_2(NO_3)}$ (3)

To a solution of **1** (0.1045 g, 0.1 mmol) in ethanol (2 mL) was added a solution of [PPh<sub>4</sub>]NO<sub>3</sub> (0.0198 g, 0.05 mmol) in ethanol (4 mL). Within 45 min, colorless crystals of complex **3** began to precipitate. After 2 h, the reaction mixture was slowly concentrated for 12 h to 1 mL, the resulting crystals of **3** were filtered off, washed with ethanol (3 × 0.5 mL) and *n*-hexane (2 × 1 mL) and dried at 20 °C in vacuum for 3 h. Yield: 0.0810 g (66%). Anal. Calcd. for C<sub>60</sub>H<sub>20</sub>F<sub>24</sub>Hg<sub>6</sub>NO<sub>3</sub>P (%): C, 28.90; H, 0.81; F, 18.29. Found: C, 28.67; H, 0.76; F, 18.07. Single crystals of **3** for the X-ray diffraction study were grown from the acetone/ethanol mixture (1:2) and were not dried in vacuum.

#### 4.7. Synthesis of $[PhNMe_3]_2\{[(o-C_6F_4Hg)_3]_2(SO_4)\}$ (4)

To a suspension of [PhNMe<sub>3</sub>]<sub>2</sub>SO<sub>4</sub>· 3H<sub>2</sub>O (0.0214 g, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added upon stirring a solution of **1** (0.1047 g, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). Within 10 min, the reaction mixture became turbid and a white powder of complex **4** began to form. After 7 h of stirring, the reaction mixture was evaporated to 3 mL, the resulting **4** was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 1 mL) and water (2 × 1 mL) and dried at 100–120 °C in vacuum for 3 h. Yield: 0.0965 g (78%). Anal. Calcd. for C<sub>54</sub>H<sub>28</sub>F<sub>24</sub>Hg<sub>6</sub>N<sub>2</sub>O<sub>4</sub>S (%): C, 26.36; H, 1.15; F, 18.53. Found: C, 26.50; H, 1.35; F, 18.40. Single crystals of **4** for the X-ray diffraction study were grown from the acetone/ ethanol mixture (1:1) and were not dried in vacuum. The crystals had composition **4** Me<sub>2</sub>CO·3EtOH according to X-ray crystallography.

# 4.8. Synthesis of $[PPh_3Me]_2\{[(o-C_6F_4Hg)_3]_2(SO_4)\}$ (5)

To a solution of macrocycle **1** (0.1084 g, 0.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 mL) was added a solution of [PPh<sub>3</sub>Me]<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O (0.0358 g, 0.05 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL). Within 30 min, the reaction mixture became turbid and colorless needles of complex **5** began to precipitate. After 4 h, the resulting **5** was filtered off, washed with CH<sub>2</sub>Cl<sub>2</sub> (3 × 0.5 mL) and dried at 20 °C in vacuum for 2 h. Yield: 0.1056 g (74%). Anal. Calcd. for C<sub>74</sub>H<sub>36</sub>F<sub>24</sub>Hg<sub>6</sub>O<sub>4</sub>P<sub>2</sub>S (%): C, 32.41; H, 1.32; P, 2.26. Found: C, 32.48; H, 1.19; P, 2.09.

#### 4.9. X-ray diffraction study

Single-crystal X-ray diffraction experiments were carried out with a Bruker SMART APEX II diffractometer (graphite monochromated Mo K $\alpha$  radiation,  $\lambda = 0.71073$  Å,  $\omega$ -scan technique, T = 100 K). The APEX II software [45] was used for collecting frames of data, indexing reflections, determination of lattice constants, integration of intensities of reflections, scaling and absorption correction while SHELXTL [46] was applied for space group and structure determination, refinements, graphics and structure reporting. The structures were solved by direct methods and refined by the full-matrix least-squares technique against  $F^2$  with the anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were placed geometrically and included in the structure factors calculations in the riding motion approximation. The main experimental and crystallographic parameters are presented in Table 4.

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#### Appendix A. Supplementary material

CCDC 926086, 926087 and 926088 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data\_request/cif.

#### References

- This term was first proposed by Hawthorne et al. X. Yang, Z. Zheng, C.B. Knobler, M.F. Hawthorne J. Am. Chem. Soc. 115 (1993) 193.
- [2] V.B. Shur, I.A. Tikhonova, in: J.L. Atwood, J.W. Steed (Eds.), Encyclopedia of
- Supramolecular Chemistry, Marcel Dekker, New York, 2004, p. 68.
- [3] T.J. Wedge, M.F. Hawthorne, Coord. Chem. Rev. 240 (2003) 111.
   [4] V.B. Shur, I.A. Tikhonova, Izv. Akad. Nauk, Ser. Khim. (2003) 2401. Russ. Chem.
- Bull, Int. Ed. Engl. 52 (2003) 2539.

- [5] M.R. Haneline, R.E. Taylor, F.P. Gabbaï, Chem. Eur. J. 21 (2003) 5188.
- [6] T.J. Taylor, C.N. Burres, F.P. Gabbaï, Organometallics 26 (2007) 5252.
- [7] J.D. Wuest, Acc. Chem. Res. 32 (1999) 81.
- [8] M.F. Hawthorne, Z. Zheng, Acc. Chem. Res. 30 (1997) 267.
- [9] I.A. Tikhonova, K.I. Tugashov, F.M. Dolgushin, A.A. Yakovenko, P.V. Petrovskii, G.G. Furin, A.P. Zaraisky, V.B. Shur, J. Organomet. Chem. 692 (2007) 953.
- [10] I.A. Tikhonova, K.I. Tugashov, F.M. Dolgushin, P.V. Petrovskii, V.B. Shur, Organometallics 26 (2007) 5193.
- [11] O. Elbjeirami, C.N. Burress, F.P. Gabbaï, M.A. Omary, J. Phys. Chem. C 111 (2007) 9522.
- [12] T.J. Taylor, O. Elbjeirami, C.N. Burress, M. Tsunoda, M.I. Bodine, M.A. Omary, F.P. Gabbaï, J. Inorg. Organomet. Polym. 18 (2008) 175.
- [13] V.N. Tsupreva, O.A. Filippov, F.M. Dolgushin, K.I. Tugashov, A.I. Krylova, V.I. Bragin, I.A. Tikhonova, V.B. Shur, L.M. Epstein, E.S. Shubina, Izv. Akad. Nauk, Ser. Khim. (2008) 2489. Russ. Chem. Bull., Int. Ed. Engl. 57 (2008) 2540.
- [14] I.A. Tikhonova, K.I. Tugashov, F.M. Dolgushin, A.A. Korlyukov, P.V. Petrovskii, Z.S. Klemenkova, V.B. Shur, J. Organomet. Chem. 694 (2009) 2604.
- [15] I.A. Tikhonova, D.A. Gribanyov, K.I. Tugashov, F.M. Dolgushin, A.F. Smol'yakov, A.S. Peregudov, Z.S. Klemenkova, V.B. Shur, Organometallics 28 (2009) 6567.
- [16] A.S. Filatov, E.A. Jackson, L.T. Scott, M.A. Petrukhina, Angew. Chem. Int. Ed. 48 (2009) 8473.
- [17] I.A. Tikhonova, D.A. Gribanyov, K.I. Tugashov, F.M. Dolgushin, A.S. Peregudov, D.Yu. Antonov, V.I. Rosenberg, V.B. Shur, J. Organomet. Chem. 695 (2010) 1949.
- [18] N.A. Semenov, I.Yu. Bagryanskaya, A.V. Alekseev, Yu.V. Gatilov, E. Lork, R. Mews, G.-V. Roeschentaler, A.V. Zibarev, Zh. Strukt. Khim. 51 (2010) 569. J. Struct. Chem. 51 (2010) 552 (Engl. Transl.).
- [19] I.A. Tikhonova, D.A. Gribanyov, K.I. Tugashov, F.M. Dolgushin, A.F. Smol'yakov, A.S. Peregudov, Z.S. Klemenkova, V.B. Shur, ARKIVOC (2011) 172.
- [20] A.S. Filatov, A.K. Greene, E.A. Jackson, L.T. Scott, M.A. Petrukhina, J. Organomet. Chem. 696 (2011) 2877.
- [21] M. Fleischmann, C. Heindl, M. Seidl, G. Balázs, A.V. Virovets, E.V. Peresypkina, M. Tsunoda, F.P. Gabbaï, M. Scheer, Angew. Chem. Int. Ed. 51 (2012) 9918.
- [22] I.A. Tikhonova, A.A. Yakovenko, K.I. Tugashov, F.M. Dolgushin, P.V. Petrovskii, M.Kh. Minacheva, B.N. Strunin, V.B. Shur, Izv. Akad. Nauk, Ser. Khim. (2013) 710; Russ. Chem. Bull. Int. Ed. Engl. 62 (2013) in press.
- [23] (a) P. Sartori, A. Golloch, Chem. Ber. 101 (1968) 2004;
   (b) M.C. Ball, D.S. Brown, A.G. Massey, D.A. Wickens, J. Organomet. Chem. 206
- (1981) 265. [24] V.B. Shur, I.A. Tikhonova, A.I. Yanovsky, Yu.T. Struchkov, P.V. Petrovskii,
- S.Yu. Panov, G.G. Furin, M.E. Volpin, J.Organomet. Chem. 418 (1991) C29. [25] V.B. Shur, I.A. Tikhonova, A.I. Yanovsky, Yu.T. Struchkov, P.V. Petrovskii,
- [25] V.D. Shui, E.K. Hildolova, A.L. Fallovsky, R.L. Stuchkov, F.V. Fertovski, S.Yu. Panov, G.G. Furin, M.E. Volpin, Dokl. Akad. Nauk SSSR 321 (1991) 1002. Dokl. Chem. 321 (1991) 391 (Engl. Transl.).
- [26] I.A. Tikhonova, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, A.N. Gavrilova, L.N. Saitkulova, E.S. Shubina, L.M. Epstein, G.G. Furin, V.B. Shur, J. Organomet. Chem. 508 (1996) 271.
- [27] E.S. Shubina, I.A. Tikhonova, E.V. Bakhmutova, F.M. Dolgushin, M.Yu. Antipin, V.I. Bakhmutov, I.B. Sivaev, L.N. Teplitskaya, I.T. Chizhevsky, I.V. Pisareva, V.I. Bregadze, L.M. Epstein, V.B. Shur, Chem. Eur. J. 7 (2001) 3783.
- [28] I.A. Tikhonova, E.S. Shubina, F.M. Dolgushin, K.I. Tugashov, L.N. Teplitskaya, A.M. Filin, I.B. Sivaev, P.V. Petrovskii, G.G. Furin, V.I. Bregadze, L.M. Epstein, V.B. Shur, Izv. Akad. Nauk, Ser. Khim. (2003) 570. Russ. Chem. Bull. Int. Ed. Engl. 52 (2003) 594.
- [29] I.A. Tikhonova, F.M. Dolgushin, K.I. Tugashov, O.G. Ellert, V.M. Novotortsev, G.G. Furin, M.Yu. Antipin, V.B. Shur, J. Organomet. Chem. 689 (2004) 82.
- [30] L.N. Saitkulova, E.V. Bakhmutova, E.S. Shubina, I.A. Tikhonova, G.G. Furin, V.I. Bakhmutov, N.P. Gambaryan, A.L. Chistyakov, I.V. Stankevich, V.B. Shur, L.M. Epstein, J. Organomet. Chem. 585 (1999) 201.
- [31] (a) A.J. Canty, G.B. Deacon, Inorg. Chim. Acta 45 (1980) L225;
  (b) P. Pyykkö, M. Straka, Phys. Chem. Chem. Phys. 2 (2000) 2489;
  (c) S.S. Batsanov, Zh. Neorg. Khim. 36 (1991) 3015;
  (d) S.C. Nyburg, C.H. Faerman, Acta Crystallogr. Sect. B 41 (1985) 274.
- [32] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, J. Chem.
- Soc. Perkin Trans. II (1987) S1.
- [33] Cambridge Structural Database, CSD Version 5.34 (November 2012).
- [34] A.A. Zinn, C.B. Knobler, D.E. Harwell, M.F. Hawthorne, Inorg. Chem. 38 (1999) 2227.
- [35] M.R. Haneline, F.P. Gabbaï, Angew. Chem. Int. Ed. 43 (2004) 5471.
- [36] I.A. Tikhonova, F.M. Dolgushin, K.I. Tugashov, P.V. Petrovskii, M.Yu. Antipin, V.B. Shur, Izv. Akad. Nauk, Ser. Khim. (2004) 2754. Russ. Chem. Bull. Int. Ed. Engl. 53 (2004) 2871.
- [37] I.A. Tikhonova, F.M. Dolgushin, A.A. Yakovenko, K.I. Tugashov, P.V. Petrovskii, G.G. Furin, V.B. Shur, Organometallics 24 (2005) 3395.
- [38] J.B. King, M.R. Haneline, M. Tsunoda, F.P. Gabbaï, J. Am. Chem. Soc. 124 (2002) 9350.
- [39] J.B. King, M. Tsunoda, F.P. Gabbaï, Organometallics 21 (2002) 4201.
- [40] I.A. Tikhonova, F.M. Dolgushin, K.I. Tugashov, G.G. Furin, P.V. Petrovskii, V.B. Shur, Izv. Akad. Nauk, Ser. Khim. (2001) 1595. Russ. Chem. Bull. Int. Ed. Engl. 50 (2001) 1673.
- [41] I.A. Tikhonova, F.M. Dolgushin, K.I. Tugashov, P.V. Petrovskii, G.G. Furin, V.B. Shur, J. Organomet. Chem. 654 (2002) 123.

- [42] J. Baldamus, G.B. Deacon, E. Hey-Hawkins, P.C. Junc, C. Martin, Aust. J. Chem. 55 (2002) 195.
- [43] Yu.K. Grishin, Yu.A. Strelenko, L.A. Margulis, Yu.A. Ustynyuk, L.S. Golovchenko, A.S. Peregudov, D.N. Kravtsov, Dokl. Akad. Nauk SSSR 249 (1979) 892. Dokl. Chem. 249 (1979) (Engl. Transl.).
- [44] C. Kahanda, O. Popovych, Aust. J. Chem. 47 (1994) 921.[45] APEX II Software Package, Bruker AXS Inc, 5465, East Cheryl Parkway, Madison, WI 5317, 2005.
- [46] SHELXTL V. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA, 1998.