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Phenylmercury(II) complexes with pyrimidine-2-thionato ligands: Synthesis and characterization

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ABSTRACT

The treatment of phenylmercury(II) acetate with several pyrimidine-2-thiones (RpymSH) results in the formation of the corresponding pyrimidine-2-thionato complexes [PhHg(RpymS)]. The crystal structure of [PhHg(4,6-Me_2pymS)] shows a nearly lineal coordination environment for the mercury atom, with the ligand using the exocyclic sulfur atom to bind the metal; a weak interaction between mercury and one of the heterocyclic nitrogens is also observed. Vibrational and ^{1}H, ^{13}C and ^{199}Hg NMR spectroscopic data of the complexes are discussed and related to the structure.

1. Introduction

The coordination chemistry of S, N donor ligands has known an increasing interest because of their potential application as models for metalloproteins [1,2]. More particularly, heterocyclic thione/thionato complexes have been considered as models for interactions of a number of biological molecules with metals [3–5]. Many metal complexes containing sulfur donor atoms have demonstrated their capability in the treatment of rheumatoid arthritis, anticancer activity or a variety of biochemical applications [6–9]. Moreover, heterocyclic thiones have been also proposed as models of adsorbent materials for the retention of heavy metals from the environment [10].

On the other hand, the coordination chemistry of organomercuric(II) cations (RHg^+; R = Ph, Me, etc.) is also very important since they show very high toxicity because of their capability to bind cysteine thiolato groups and so, detoxificating agents are required [11]. Despite this, only a few studies on the interaction between heterocyclic thiones and organomercuric(II) compounds have been reported [12–15].

In this paper we report the synthesis of several phenylmercury(II) complexes with different pyrimidine-2-thionato ligands (see Scheme 1) and their characterization by analytical and spectroscopic methods. The crystal structure of [PhHg(4,6-Me_2pymS)] is also presented.

2. Experimental

2.1. Materials

Pyrimidine-2-thione, 4,6-dimethylpyrimidine-2-thione, 4-trifluoromethyl pyrimidine-2-thione, thiourea, 1,1,1-trifluoro-2,4-pentanedione and phenylmercury(II) acetate are commercial products and were used without further purification.

2.2. Instrumentation

Elemental analysis were performed with a Carlo–Erba EA microanalyser. IR spectra were recorded as KBr mulls on a Bruker IFS-66V spectrophotometer. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker AMX 300 MHZ instrument with $CDCl_3$ as solvent. Chemical shifts are given relative to TMS as the internal standard. ^{199}Hg NMR spectra were recorded on a Bruker AMX500 spectrophotometer with $CDCl_3$ as solvent. The mass spectra (FAB) were recorded on a Micromass Autospec spectrometer, with 3-nitrobenzyl alcohol as the matrix material. X-ray data were collected on a Bruker Smart CCD 1000 diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The data were collected at T = 293 K. The ω-scan technique was employed to measure intensities. Decomposition of the crystal did not occur during the data collection. The intensities of all of the data were corrected for Lorentz and polarisation effects. Absorption corrections were carried out using SADABS [16]. The structure was solved by direct methods and refined [17] by full-matrix least squares based on F^2. Hydrogen atoms were also included in idealised positions and refined with isotropic displacement parameters. Atomic

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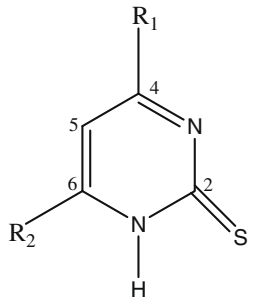

pymSH: $R_1 = R_2 = H$

4,6-Me_2pymSH: $R_1 = R_2 = Me$

4,6-CF_3MepymSH: $R_1 = CF_3$; $R_2 = Me$

4-CF_3pymSH: $R_1 = CF_3$; $R_2 = H$

Scheme 1. General structure for the thiones.

scattering factors and anomalous dispersion for all of the atoms were taken from the International Tables for X-ray Crystallography [18]. The crystal data and summary of data collection are given in Table 2. An ORTEP 3 drawing [19] along with the numbering scheme used is provided in the text.

2.3. Synthesis

4-Trifluoromethyl, 6-methylpyrimidine-2-thione is not a commercial product and was obtained as previously reported [20]

The syntheses of all of the complexes were carried out at room temperature following all of the safety measures related to the toxicity of organomercuric(II) complexes. At the end of every synthesis an acetic acid odour was observed.

2.3.1. [PhHg(pymS)] (**1**)

0.1 g of thione (0.89 mmol) dissolved in acetone were added to a suspension of [PhHg(AcO)] in the same solvent (300 mg, 0.89 mmol). A colourless solution was obtained immediately and the mixture was stirred at room temperature for 2 h. A little amount of solid in suspension appeared, so the mixture was filtered off and the solid was rejected. The solvent was removed by distillation under vacuum and a white powder was obtained. It was washed with diethyl ether and dried. Yield: 289 mg (83.4%). Anal. Calc. for $C_{10}H_8N_2SHg$: C, 30.92; N, 7.21; H, 2.06; S, 8.24. Found: C, 30.50; N, 7.28; H, 2.03; S, 8.23%. IR (KBr, cm^{-1}): 3021 (m), 1564 (s), 1542 (s), 1477 (m), 1457 (w), 1424(m), 1204 (m), 1175 (s), 1087 (w), 1072 (w), 1057 (w), 1025 (m), 997 (w), 982 (w), 962 (w), 939(w), 921 (w), 906 (w), 794 (m), 767 (m), 748 (s), 728 (s), 694 (m), 668 (w), 634 (m), 476 (w), 456 (m), 444 (w). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.25 (d, 1H, H_6); 7.27 (d, 1H, H_4); 7.11–7.15 (multiplet, phenyl protons); 6.85 (dd, 1H, H_5; $^3J(H_5H_6)$ = 4.92 Hz; $^3J(H_5H_4)$ = 3.06 Hz. ^{13}C NMR-{1H} (300 MHz, $CDCl_3$, ppm): δ = 157.88 (s, C_4/C_6); 129.10–136.53 (phenyl carbons); 116.74 (s, C_5). ^{199}Hg-RMN (500 MHz, $CDCl_3$, ppm): δ = −1186 ppm. MS (FAB): m/z = 389 (M^+) 25.7%; 309 (SHgPh) 2.8%.

2.3.2. [PhHg(4,6-Me_2pymS)](**2**)

A solution of 4,6-dimethylpyrimidine-2-thione (0.1 g, 0.71 mmol) in acetone was added dropwise to a suspension of phenylmercury(II) acetate (240 mg, 0.71 mmol) in the same solvent. The suspension became a colourless solution and was stirred for 2 h at room temperature. The solvent was removed by distillation under vacuum and a white solid was obtained. This solid was washed with Et_2O and dried. Yield: 240 mg (81.1%). Anal. Calc. for $C_{12}H_{12}N_2SHg$: C, 34.61; N, 6.73; H, 2.88; S, 7.69. Found: C, 34.61; N, 6.85; H, 2.89; S, 7.69%. IR (KBr, cm^{-1}): 3043 (m), 2920 (w), 1578 (s), 1524 (s), 1499 (m), 1477 (m), 1428 (m), 1384 (m), 1364 (m), 1353 (w), 1357 (m), 1305 (w), 1251 (s), 1187 (w), 1175 (w), 1155 (w), 1093 (w), 1061 (w), 1031 (w), 1021 (w), 1008 (w), 996 (w), 975 (w), 890 (w), 871 (w), 848 (w), 840 (w), 760 (w), 723 (m), 692 (m), 590 (w), 562 (w), 546 (m), 447 (m). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.30–7.43 (multiplet, phenyl protons); 6.72 (s, 1H, H_5); 1.58 (s, broad; 6H, methyl protons). ^{13}C NMR-{1H} (300 MHz, $CDCl_3$, ppm): 166.62 (s, C_2); 149.56 (s, C_4/C_6); 136.52–121.13 (phenyl carbons); 116.00 (s, C_5); 24.01 (s, methyl groups). ^{199}Hg-RMN (500 MHz, $CDCl_3$, ppm): δ = −1228 ppm. MS (FAB): m/z = 756 [PhHg(4,6-Me_2pyms)$_2$Hg]; 416 (M^+) 27.9%; 215 (4,6-Me_2pymSPh) 8.9%; 139 (4,6-Me_2pymS) 17.8%. Crystals suitable for X-ray diffraction studies were obtained by crystallization from acetone.

2.3.3. [PhHg(4,6-CF_3MepymS)](**3**)

0.1 g (0.51 mmol) of 4,6-CF_3MepymSH were dissolved in acetone and this solution was added dropwise to a suspension of phenylmercury(II) acetate (173 mg, 0.51 mmol) in the same solvent. The initial suspension became a pale yellow solution instantaneously and the mixture was stirred at room temperature for 2 h. The solvent was then removed under vacuum and a white solid, which was washed with hexane and dried. Yield: 206 mg (85.8%). Anal. Calc. for $C_{12}H_9N_2F_3SHg$: C, 30.61; N, 5.95; H, 1.93; S, 6.81. Found: C, 29.95; N, 5.81; H, 1.75; S, 6.81%. IR (KBr, cm^{-1}): 3040 (w), 1581 (m), 1544 (m), 1385 (s), 1366 (s), 1308 (w), 1266 (s), 1227(m), 1199 (m), 1173 (m), 1141(s), 1112 (s), 1012 (m), 979 (w), 921 (w), 866 (w), 847 (m), 835 (m), 781 (m), 730 (w), 709 (s), 616 (w), 575 (w), 550 (m), 516 (w), 466 (m), 416 (w), 365 (m), 343 (w). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 7.60 (s, 1H, H_5); 6.90–7.40 (multiplet, phenyl protons); 2.22 (s, 3H, methyl protons). ^{13}C NMR-{1H} (300 MHz, $CDCl_3$, ppm): 176.12 (s, C_2); 168.08 (s, C_6); 138.47–126.86 (phenyl carbons); 99.99 (s, C_5); 13.99 (s, CH_3). ^{199}Hg-RMN (500 MHz, $CDCl_3$, ppm): δ = −1232 ppm. ^{19}F NMR ($CDCl_3$, 300 MHz, ppm): δ = −100.28 (s). MS (FAB): m/z = 546 [PhHg(4,6-CF_3MepymS)Hg] 1.9%; 470 (M^+) 13.7%: 393 [(4,6-CF_3MepymS)Hg] 1.81%.

2.3.4. [PhHg(4-CF_3pymS)](**4**)

0.186 g (5.55 mmol) of phenylmercury(II) acetate were suspended in acetone. A solution containing 0.1 g (0.55 mmol) of thione was added dropwise to the former mixture affording a colourless solution. It was stirred for 2 h at room temperature and the solvent was removed at low pressure. The white solid obtained was washed with ether and dried. Yield: 237 mg (93.5%). Anal. Calc. for $C_{11}H_7N_2F_3SHg$ (%): C, 28.82; N, 6.11; H,1.54; S, 6.98. Found: C, 28.44; N, 5.98; H, 1.44; S, 7.01%. IR (KBr, cm^{-1}): 3041 (m), 1561 (s), 1503 (w), 1478 (m), 1426 (s), 1333 (s), 1208(s), 1172 (m), 1148(s), 1115(s), 1083 (w), 1062 (w), 1022 (m), 997 (w), 878 (w), 918 (w), 865 (w), 835 (s), 781 (w), 732 (s), 697 (m), 678 (w), 668 (s), 473 (w), 451 (m), 436 (w), 422 (w). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ = 8.67 (d, 1H, H_5; $^3J(H_5H_6)$ = 4.75 Hz); 7.37–7.46 (multiplet, phenyl protons); 7.32 (d, 1H, H_6). ^{13}C NMR-{1H} (300 MHz, $CDCl_3$, ppm): δ = 175.81 (s, C_2); 159.21 (s, C_6); 129.32–136.34 (Phenyl carbons); 112.30 (s, C_5). ^{19}F NMR ($CDCl_3$, 300 MHz, ppm): δ = −70.57 (s). MS (FAB): m/z = 1113 [Hg(HgPh)$_2$(4-CF_3ppymS)$_2$] 15.8%; 935 [(PhHg)$_2$(4-CF_3ppymS)Hg] 7.9%; 735 [(PhHg)$_2$(4-CF_3ppymS)] 54.8; 456 (M^+) 57.5%; 255 [4-CF_3pymS-Ph] 100%.

3. Results and discussion

3.1. General

Neutral complexes of formula [PhHg(RpymS)] have been obtained in reasonable yields (81–94%) by reaction of phenylmercury(II) acetate with several pyrimidine-2-thiones.; the thiones

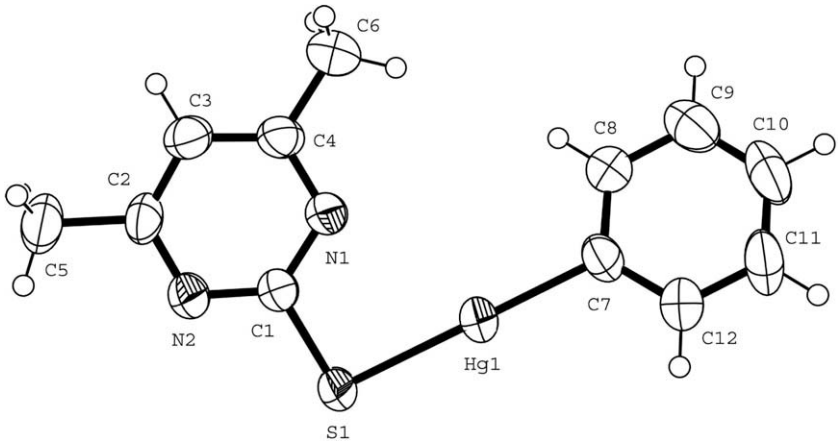

Fig. 1. Crystal structure of [PhHg(4,6-Me_2pymS)] (**2**).

displaced the acetate ligand from the mercury coordination sphere and became anionic thionato species.

3.2. Crystal structure of [PhHg(4,6-Me_2pymS)] (**2**)

Fig. 1 shows the crystal structure of complex **2** together with the labelling scheme used. Main bond lengths and angles are given in Table 1.

The crystal structure of this complex consists of mononuclear discrete molecules (two per asymmetric unit) with the ligand showing basically a monodentate behaviour; the thionato ligand binds the metal centre through the exocyclic sulfur atom. However, a very weak interaction between the mercury atom and one of the heterocyclic nitrogen atoms is also observed (see below). The mercury atom presents a pseudo SHgC linear coordination environment with SHgC bond angles showing very small deviations from the ideal value (178.6(3)° and 178.5(3)°). This angle is a little bigger than that found for the phenylmercury(II) complex containing the corresponding neutral thione (4,6-Me_2pymSH) [14] and the dimeric complex of phenylmercury(II) with pyridine-2-thionato [15]. A dimeric dithiouracilato pheylmercury(II) complex [14] shows quite similar values: 178.3(4) and 175.2(4)°.

The Hg–S bond lengths are 2.379(2) and 2.363(2) Å, which are quite similar to those found for the mentioned complex [14] with the neutral thione (2.367(2) Å), the dimeric complex [15] derived from pyridine-2-thionato (2.376(3)–2.380(3) Å) and the previously mentioned phenyl mercury(II) complex with dithiouracilato [14]. They are also quite similar to those found in [Hg(3-CF_3py$S)_2$] [21] (2.3642(18)–2.3761(17) Å) and in the thiosemicarbazone derivative [Hg($C_6H_5C_5H_4N$)(Hstsc)] [22] (2.357(2) Å). The Hg–S bond lengths observed for **2** are shorter than that found for the methyl mercury derivative [MeHg(pymS)] [23] (2.39(2) Å) which also contains a pyrimidine-2-thionato ligand. However, they are longer than those found in several Hg(II) thionato complexes as [Hg(4,6-CF_3MepymS$)_2$]: 2.330(2) Å [24] and [Hg(5-CF_3py$S)_2$]: 2.319(3) Å [21]. The values observed for complex **2** fall within the range defined by the distances observed for [Hg(Tab$)_2$]($PF_6)_2$ (2.331(3) Å, Tab = 4-trimethylamoniobenzenethiolato) [25] and [Hg_2(Tab$)_6]_3$-(PF_6)Cl_{11} (2.787(12) Å) [25].

The Hg(1)–N(1) and Hg(2)–N(3) distances are 2.785(7) and 2.773(7) Å, respectively. These distances are shorter than the sum of their van der Waals radii of N and Hg (1.73 [26] and 1.55 Å [27] for Hg and N, respectively), which indicates that a weak interaction between Hg and one of the heterocyclic nitrogen atoms occurs. The distances obtained for **2** are shorter than those found for other organomercurial derivatives containing heterocyclic thioamidato ligands [14,15,23,28], neutral thioamides [14] or even simple mercury(II) complexes with thionato ligands [21,24,29]. They are also shorter than that observed for a phenylpyridine cyclometallated mercury(II) complex containing a thiosemicarbazone ligand [22]. All of the mentioned complexes are proposed as examples for Hg···N weak interactions.

The observed C–S bond lengths are (1.747(8) and 1.755(9) Å) are intermediate between those observed for the free ligands 4,6-dimethylpyrimidine-2-thione [30] and 4,6-dimethyl-1-phenylpyrimidine-2-thione [31] (1.392(2) and 1.686(4) Å respectively) which exist in the thione form in the solid state, and the values of

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

Hg(1)–C(7)	2.073(8)	Hg(2)–C(19)	2.065(8)
Hg(1)–S(1)	2.378(2)	Hg(2)–S(2)	2.363(2)
Hg(1–N(1)	2.785(3)	Hg(2)–N(3)	2.773(5)
S(1)–C(1)	1.747(8)	S(2)–C(13)	1.755(9)
C(7)–Hg(1)–S(1)	178.6(2)	C(19)–Hg(2)–S(2)	178.6(2)

Table 2
Crystal data and structure refinement for **2**.

Empirical formula	$C_{24}H_{24}Hg_2N_4S_2$
Formula mass	833.77
Crystal system	Monoclinic
Space group	*P*2(1)/c
a (Å)	14.583(3)
b (Å)	14.202(3)
c (Å)	12.436(3)
α (°)	90
β (°)	102.546(4)
γ (°)	90
V (Å^3)	2414.2(9)
Z	4
D_{calc} (Mg m^{-3})	2.203
μ (Mo Kα) (mm^{-1})	12.383
F(0 0 0)	1552
Crystal size (mm)	0.50 × 0.18 × 0.18
T (K)	293(2)
Number of reflections collected	28 926
Number of independent reflections	5169
Goodness-of-fit (GOF) on F^2	1.087
R[a]	0.0331
Rw[b]	0.0658

[a] $R = [||F_o| - |F_c||]/[|F_o|]$.
[b] $Rw = [(F_o^2 - F_c^2)]/(F_o^2)]^{1/2}$.

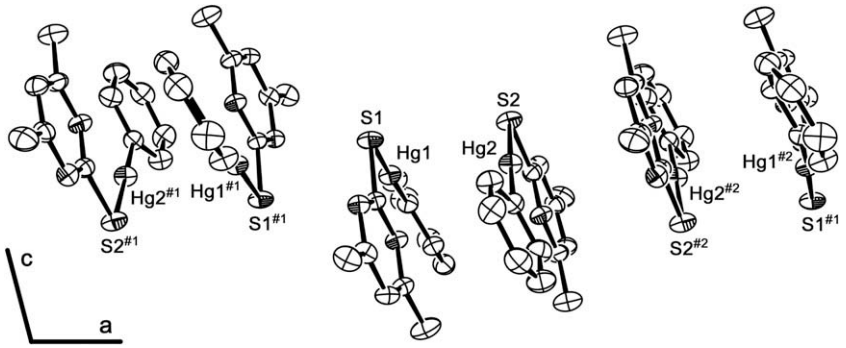

Fig. 2. Crystal packing diagram for [PhHg(4,6-Me_2pymS)] along the *a* axis. (Symmetry codes: #1: $-x$, $-y+1$, $-z+2$; #2: $-x+1$, $-y+1$, $-z+2$).

1.781(2) and 1.782(3) Å found for bis(pyrimidyl)-2,2′-disulfide [32] and bis(4,6-dimethylpyrimidyl) disulfide [33], which posses a simple C–S bond. This confirms that the ligand acts as a pyrimidine-2-thionato rather than the neutral thione.

The distance between two Hg atoms of two neighbouring molecules is 3.9035(8). This value is in the upper limit of the range of the sum of the van der Waals radii (1.7–2.0 Å) [26]. It is also quite longer than those reported for elemental mercury (3.02 Å) [34], mercury(0) clusters (2.797(2)–3.820(2) Å) [35], dinuclear mercury (I) complexes (Hg_2^{2+}, 2.5 Å) [36] or the tris(1,3-dimethyluracil-5-yl)mercurioxonium salt, which dimerises in two different ways through weak Hg···Hg contacts [Hg···Hg distances in the range 3.4552(6) to 3.5974(5) Å) [37]. The observed Hg···Hg distance is also much longer than that reported for methyl(2-mercapto-4-metylpyrimidinato)mercury(II) (3.101(2) Å) [38]. It is also longer than those found in many other mercury(II) complexes (3.848–3578 Å) [39–43]. Thus, we conclude that if any Hg···Hg interaction occurs it must be extremely weak.

3.3. Crystal packing

The asymmetric unit of the crystal lattice contains two mercury complexes, with the aromatic rings almost parallel to each other. The mercury–mercury distance for this pair of complexes is 3.9035(8) Å. The aromatic rings of one complex establish very weak π-stacking interactions with the aromatic rings of the other complex (centroid–centroid distances: pyrimidine1···phenyl2 = 3.799(5) Å, phenyl1···pyrimidine2 = 3.980(5) Å). This pair of complexes establishes very weak van der Waals interactions with neighbouring pairs of complexes. Thus, the complexes are arranged in pairs that zig–zag along the crystallographic *a* axis with the aromatic rings almost parallel to one another, as shown in Fig. 2. This arrangement leaves the sulfur atoms pointing up and down the crystallographic *c* axis. These atoms establish very weak C–H···S interactions, connecting the zigzag rows in the *c* direction. These rows of complexes (Fig. 2) are also connected to other rows in the *b* direction, although in this case these interactions are weaker van der Waals H···H contacts.

3.4. Spectroscopic studies

The IR spectra of the complexes do not show bands due to υ_{N-H}, which in the free ligands appear at 3200–2050 cm^{-1}; this fact provides evidence of the deprotonation of the thiones during the formation of the complexes, thereby confirming that the ligand acts as a thionato species. This conclusion is supported by the presence of a very strong band attributable to $\nu_{C=C}$ and $\nu_{C=CN}$ in the range 1561–1568 cm^{-1}. These bands are shifted to lower wavenumbers with respect to their position in the spectra of the free ligands (1650–1550 cm^{-1}). This seems to confirm the presence of weak Hg···N interactions in all complexes [44,45]. The spectra of the complexes also show additional bands which are assigned to the ring breathing vibration in the region 1190–995 cm^{-1} and 750–620 cm^{-1}. All of the spectra show relatively intense bands at 1250–1180 cm^{-1}, which is the typical region for C=S double or partially double bonds [46,47]. The spectra of the complexes containing methyl groups also show additional medium intensity bands in the range 3100–2900 cm^{-1}, which correspond to the vibrations of these groups.

The mass spectra of all complexes show peaks due to the molecular ion with the expected isotopic distribution. Furthermore, signals due to the loss of phenyl fragment or the rearrangement of the ligands to give RpymS-Ph are also observed.

The ^{1}H NMR spectra of these complexes do not show the signal attributable to NH group; this confirms deprotonation of the ligands and the presence of thionato species in the complexes. All of them show a multiplet attributable to the phenyl protons and the corresponding aromatic signals which are assigned to the ligands. The spectrum of complex **1** shows three signals for the pyrimidinic protons. The fact that H_4 and H_6 show different frequencies for their resonances, indicates that they're not equivalent; so it seems to confirm the presence of a Hg–N interaction also in solution. For **2** and **3** signals attributable to methyl groups are also observed. In complex **2** the corresponding signal is observed as a broad singlet, which again supports the presence of a Hg–N interaction. As expected the ^{199}Hg NMR spectra of the complexes show one signal; the frequencies for all of them are quite similar to those found for several organomercurial complexes containing neutral thioamides [14] or thionatos [28]; the values are also similar to those found for several mercury(II) complexes with pyridine-2-thionato [21] or pyrimidine-2-thionato ligands [24]. For complexes **3** and **4**, ^{19}F NMR spectra show the expected signal (−100 and −70 ppm respectively); these frequencies are in agreement with those reported for several metallic complexes with heterocyclic ligands containing $-CF_3$ groups [48–50].

Acknowledgements

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Appendix A. Supplementary material

CCDC 758813 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.02.022.

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