Journal of Organometallic Chemistry 695 (2010) 1271–1275

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

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

Antonio Rodríguez [a,*], Antonio Sousa-Pedrares [b], José A. García-Vázquez [b], Jaime Romero [b], Antonio Sousa [b]

[a] Departamento de Química Fundamental, Universidade da Coruña, 15071-A Coruña, Spain
[b] Departamento de Química Inorgánica, Universidade de Santiago de Compostela, 15782-Santiago de Compostela, Spain

ARTICLE INFO

Article history:
Received 23 December 2009
Received in revised form 12 February 2010
Accepted 18 February 2010
Available online 24 February 2010

Keywords:
Organomercurials
Heterocycles
S ligands

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.

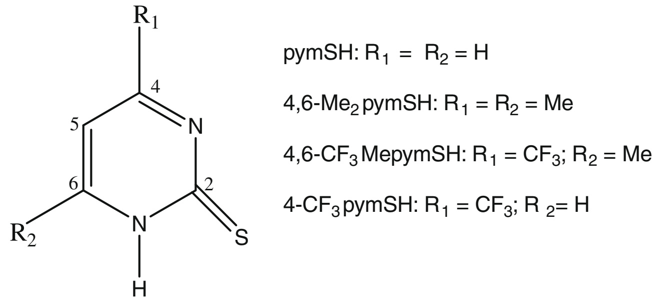
2.2. Instrumentation

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

---

[*] Corresponding author.
E-mail address: antonio.rodriguezl@udc.es (A. Rodríguez).

0022-328X/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2010.02.022



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). ^1H NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 8.25$ (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): $\delta = 157.88$ (s, C_4/C_6); 129.10–136.53 (phenyl carbons); 116.74 (s, C_5). ^{199}Hg-RMN (500 MHz, $CDCl_3$, ppm): $\delta = -1186$ ppm. MS (FAB): $m/z = 389$ (M^+) 25.7%; 309 (SHgPh) 2.8%.

2.3.2. [PhHg(4,6-Me$_2$pymS)](**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). ^1H NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.30$–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): $\delta = -1228$ ppm. MS (FAB): $m/z = 756$ [PhHg(4,6-Me$_2$pyms)$_2$Hg]; 416 (M^+) 27.9%; 215 (4,6-Me$_2$pymSPh) 8.9%; 139 (4,6-Me$_2$pymS) 17.8%. Crystals suitable for X-ray diffraction studies were obtained by crystallization from acetone.

2.3.3. [PhHg(4,6-CF$_3$MepymS)](**3**)

0.1 g (0.51 mmol) of 4,6-CF$_3$MepymSH 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). ^1H NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 7.60$ (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): $\delta = -1232$ ppm. ^{19}F NMR ($CDCl_3$, 300 MHz, ppm): $\delta = -100.28$ (s). MS (FAB): $m/z = 546$ [PhHg(4,6-CF$_3$MepymS)Hg] 1.9%; 470 (M^+) 13.7%: 393 [(4,6-CF$_3$MepymS)Hg] 1.81%.

2.3.4. [PhHg(4-CF$_3$pymS)](**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). ^1H NMR ($CDCl_3$, 300 MHz, ppm): $\delta = 8.67$ (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): $\delta = 175.81$ (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): $\delta = -70.57$ (s). MS (FAB): $m/z = 1113$ [Hg(HgPh)$_2$(4-CF$_3$ppymS)$_2$] 15.8%; 935 [(PhHg)$_2$(4-CF$_3$ppymS)Hg] 7.9%; 735 [(PhHg)$_2$(4-CF$_3$ppymS)] 54.8; 456 (M^+) 57.5%; 255 [4-CF$_3$pymS-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