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Synthesis, characterization and structural study of mercury(II) complexes with fluoroalkylthiocarbamates

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ABSTRACT

Ten new mercury (II) complexes (**1**–**10**) were synthesized from the reaction of mercury (II) chloride with *O*-*F*-alkylated thiocarbamates. These compounds were fully characterized by multinuclear (^{1}H, ^{19}F, ^{13}C and ^{199}Hg) NMR and IR spectroscopic techniques, HRMS and in one case (complex **3**) by X-ray crystallography. The absence of NH proton (^{1}H) and C=S (^{13}C) NMR signals as well as the presence of C=N (^{13}C) and S-Hg (^{199}Hg) NMR signals for complexes **1**–**10** suggest that the thiocarbamate ligand is coordinated to the mercury center through its sulfur atom. This was further confirmed by X-ray crystallographic data obtained for complex **3**.

1. Introduction

Metal complexes of anionic thiocarbamate ester ligands with the general formula ArN=C(S)OR have been known since the 1970's. The majority of them were obtained by insertion reactions of aryl isothiocyanates into metal-alkoxide bonds. For instance, the mercury (II) complex [Hg{PhN = C(S)OMe}$_2$] was prepared from Hg(OMe)$_2$ and PhNCS [1]. Different methods were then described and showed the ability of thiocarbamates (TCs) to form stable complexes with metal ions including rhodium, iridium, palladium, platinum, and gold [2]. They can also be used as sulfhydryl group antidotes which may have potential applications in medical or marine environmental systems due to their high affinity to heavy metal ions such as Hg^{2+} and Pb^{2+}[3,4]. In addition, the strong affinity and selectivity of TCs triggered their use as ore flotation reagents. For example, *O*-isopropyl-*N*-ethylthiocarbamate was found to be more selective for copper sulfide against gangue iron sulfides and can thus be used as collectors for copper/iron flotation separation [5]. In order to improve flotation performance of such TCs, many research groups have studied the effect of *O*-substituent and *N*-substituent groupings on the collecting properties of TCs [6–9] and ethoxycarbonylthionocarbamates as flotation collectors were developed by Cytec Industries Inc. These TCs were previously shown to be powerful collectors for chalcopyrite and very selective against pyrite in alkaline and neutral pH conditions [10–21]. Recently, some research groups reported on the substituted thiocarbamate complexes with mercury in order to investigate the potential utility of such TCs for medical or marine detoxification through introduction of glycosyl and other biologically active groups [22–24]. Surprisingly and despite the importance of fluorine-containing molecules as the strong electron-withdrawing effect of fluorine contributes to extraordinary functional properties and numerous applications, little work was reported on fluoroalkylthiocabamates [25].

More recently, we have reported on the synthesis of a series of *O*–*F*-alkyl thiocarbamates and their stereochemistry in solution [26]. Herein, we explore the coordination properties of these TCs towards mercury chloride and show that the majority of them form stable complexes with Hg^{2+}. These new complexes were fully characterized by multinuclear (^{1}H, ^{13}C, ^{19}F and ^{199}Hg) NMR, IR and HRMS.

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2. Experimental

2.1. Reagents and methods

All solvents and chemicals were reagent grade and used as received. TMS was used as the internal standard for ^{1}H and ^{13}C and $CFCl_3$ for ^{19}F NMR spectroscopy. and ^{1}H, ^{13}C, ^{19}F, ^{199}Hg NMR spectra were recorded on a Bruker 300 MHz in $CDCl_3$. Infrared spectra were recorded on a VERTEX 70 FT-IR spectrometer. High mass spectrometry investigations (HRMS) were performed using a high resolution MicromassmicrOTOF-Q II 10027 spectrometer.

Caution: Because of the toxicity of mercury and related compounds, all the reactions were carried out under strong ventilation and the use of metallic apparatus was strictly avoided.

2.2. X-ray diffraction

Crystals of complex **3** suitable for X-ray analysis were obtained from an ethanol solution. X-ray diffraction data were collected using a Kappa X8 APEX II Bruker diffractometer with graphite-monochromated$Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). Crystals of complex **3**were mounted on a CryoLoop (Hampton Research) with Paratone-N oil (Hampton Research) as cryoprotectant and then flashfrozen in a nitrogen-gas stream at 100 K. The temperature of the crystal was maintained at the selected value (100 K) by means of a 700 series Cryostream cooling device to within an accuracy of ±1 K. Data collection, reduction, structure solution, and refinement were performed using the Bruker Apex2 suite (v2.0–2) [27]. Reflections were then corrected for absorption, interframe scaling, and other systematic errors with SADABS 2004/1 [28]. The structures were solved by direct methods using SIR-97 [29] and refined against F^2 by full-matrix least-squares techniques using SHELXL-2013 [30] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were located on a difference Fourier map and introduced into the calculations as a riding model with isotropic thermal parameters. All calculations were performed by using the Crystal Structure crystallographic software package WINGX [31].

2.3. General procedure for the preparation of thiocarbamate mercury complexes (**1**–**10**)

To a solution of the perfluoroalkylated thiocarbamate (1 mmol) in 20 mL of THF was added at room temperature triethylamine (1.5 mmol). The mixture was stirred for 30 min, then $HgCl_2$ (0.14 g, 0.5 mmol) was added. The reaction mixture was stirred at 0–35 °C for 2–5 h the crude products were purified with column chromatography on silica gel (70–230 mesh) using dry chloroform (100%) as eluent and recrystallized from ethanol to give compounds **1**–**10**.

2.3.1. Bis[O-2-perfluorohexylethyl- N-(4-nitrophenyl) thiocarbamato)]mercury(II) (**1**)

Yellow powder. M.p. 81 °C. IR (cm^{-1}) 1626 (ν N=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.52 (tt, 2H, $^{3}J_{H-H} = 6$ Hz, $^{3}J_{H-F} = 18$ Hz, CH_2-CF_2), 4.60 (t, 2H, $^{3}J_{H-H} = 6$ Hz, CH_2-O), 6.87–8.17 (AA'XX' sys, 4H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 30.38 (t, $\underline{C}H_2-CF_2$, $^{2}J_{C-F} = 21$ Hz), 61.40 (s, CH_2-O), 103.15–117.21 (m, C–F), 121.89, 125.06, 144.37, 154.03 (4s, Ar–C), 160.71 (C=N). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = −80.76 (t, 3F, $^{3}J_{F-F} = 10$ Hz, CF_3), −113.10 (m, 2F, CF_2), −121.83 (m, 2F, CF_2), −122.87(m, 2F, CF_2), −123.51 (m, 2F, CF_2), −126.15 (m, 2F, CF_2). ^{199}Hg NMR (300 MHz, $CDCl_3$) δ(ppm) = −1011.76. HRMS (ESI), *m/z*: calc. for $C_{30}H_{16}F_{26}HgN_4O_6S_2Na^+$ 1310.9695 $[M+Na]^+$; found 1310.9727.

2.3.2. Bis[O-2-perfluorooctylethyl-N-(4-nitrophenyl) thiocarbamato)]mercury(II) (**2**)

Yellow powder. M.p. 89 °C. IR (cm^{-1}) 1632 (ν N=C). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 2.64 (tt, 2H, $^{3}J_{H-H} = 6$ Hz, $^{3}J_{H-F} = 18$ Hz, $\underline{C}H_2-CF_2$), 4.59 (t, 2H, $^{3}J_{H-H} = 6$ Hz, CH_2-O), 7.00–8.20 (AA'XX' sys, 4H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 30.49 (t, $\underline{C}H_2-CF_2$, $^{2}J_{C-F} = 21$ Hz), 60.84 (s, CH_2-O), 105.98–118.13 (m, C–F), 122.38, 124.87, 143.71, 155.38 (4s, Ar–C), 160.90 (C=N). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = −80.89 (t, 3F, $^{3}J_{F-F} = 10$ Hz, CF_3), −113.34 (m, 2F, CF_2), −121.79 (m, 2F, CF_2), −122.00 (m, 4F, $2CF_2$), −122.85 (m, 2F, CF_2), −123.48 (m, 2F, CF_2), −126.23 (m, 2F, CF_2). ^{199}Hg NMR (300 MHz, $CDCl_3$) δ (ppm) = −1033.34. HRMS (ESI), *m/z*: calcd. for $C_{30}H_{16}F_{34}HgN_4O_6S_2Na^+$ 1510.9569 $[M+Na]^+$; found 1510.9533.

2.3.3. Bis[O-perfluorohexyl-N-(4-trifluoromethoxyphenyl) thiocarbamato]mercury(II) (**3**)

Colorless needles; decompose at 91 °C. IR (cm^{-1}) = 1618 (ν N=C). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.57 (tt, 2H, $^{3}J_{H-H} = 6$ Hz, $^{3}J_{H-F} = 18$ Hz, $\underline{C}H_2-CF_2$), 4.64 (t, 2H, $^{3}J_{H-H} = 6$ Hz, CH_2-O), 6.83–7.23 (AA'XX' sys, 4H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 30.35 (t, $\underline{C}H_2-CF_2$, $^{2}J_{C-F} = 22$ Hz), 60.85 (s, CH_2-O), 103.26–118.81 (m, C–F), 122.22, 122.40, 146.02, 146.92 (4s, Ar–C), 157.51 (C=N). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = −58.11 (s, 3F, CF_3-O), −80.81 (t, 3F, $^{3}J_{F-F} = 9$ Hz, CF_3), −113.20 (m, 2F,CF_2), −121,85 (m, 2F, CF_2), −122,83 (m, 2F,CF_2), −123,55 (m, 2F,CF_2), −126,17 (m, 2F,CF_2). ^{199}Hg NMR (300 MHz, $CDCl_3$) δ (ppm) = −1029.23. HRMS (ESI), *m/z*: calcd. for $C_{32}H_{16}F_{32}HgN_2O_4S_2Na^+$ 1388.9640 $[M+Na]^+$; found 1388.9640.

2.3.4. Bis[O-perfluorooctyl-N-(4-trifluoromethoxyphenyl) thiocarbamato]mercury(II) (**4**)

Colorless needles; decompose at 94 °C. IR (cm^{-1}) = 1634 (ν N=C). ^{1}HNMR (300 MHz, $CDCl_3$) δ (ppm) = 2.60 (tt, 2H, $^{3}J_{H-H} = 6$ Hz, $^{3}J_{H-F} = 18$ Hz, $\underline{C}H_2-CF_2$), 4.66 (t, 2H, $^{3}J_{H-H} = 6$ Hz, CH_2-O), 6.83–7.24 (AA'XX'Sys, 4H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 30.44 (t, $\underline{C}H_2-CF_2$, $^{2}J_{C-F} = 22$ Hz), 60.93 (s, CH_2-O), 100.56–119.47 (m, C–F), 122.25, 122.39, 146.09, 146.89 (4s, Ar–C), 157.34 (C=N). ^{19}F NMR (282 MHz, $CDCl_3$) δ (ppm) = −58.16 (s, 3F, CF_3-O), −80.87 (t, 3F, $^{3}J_{F-F} = 10$ Hz, CF_3), −113.24 (m, 2F,CF_2), −121,71 (m, 2F, CF_2), −121,97 (m, 4F,2 CF_2), −122,81 (m, 2F,CF_2), −123,54 (m, 2F,CF_2), −126,22 (m, 2F, CF_2). ^{199}Hg NMR (300 MHz, $CDCl_3$) δ:-1018.95. HRMS (ESI), *m/z*: calcd. for $C_{36}H_{16}F_{40}HgN_2O_4S_2Na^+$ 1566.9694 $[M+Na]^+$; found 1566.9642.

2.3.5. Bis[O-2-perfluorohexylethyl-N-(phenyl)thiocarbamato] mercury(II) (**5**)

White powder; decomposes at 87 °C. IR (cm^{-1}) 1635 (ν N=C). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.57 (tt, 2H, $^{3}J_{H-H} = 6$ Hz, $^{3}J_{H-F} = 18$ Hz, $\underline{C}H_2-CF_2$), 4.58 (t, 2H, $^{3}J_{H-H} = 6$ Hz, CH_2-O), 6.65–7.39 (m, 5H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 30.47 (t, $\underline{C}H_2-CF_2$, $^{2}J_{C-F} = 22$ Hz), 60.73 (s, CH_2-O), 108.21–119.13 (m, C–F), 121.14, 125.05, 130.41, 149.03 (4s, Ar–C), 158.29 (C=N). ^{19}F NMR (282 MHz, $CDCl_3$) δ:-80.86 (t, 3F, $^{3}J_{F-F} = 9$ Hz, CF_3), −113.43 (m, 2F, CF_2), −121.91 (m, 2F, CF_2), −122.92 (m, 2F, CF_2), −123.59 (m, 2F, CF_2), −126.21(m, 2F,CF_2). ^{199}Hg NMR (300 MHz, $CDCl_3$) δ (ppm) = −897.32. HRMS (ESI), *m/z*: calcd. for $C_{30}H_{18}F_{26}HgN_2O_2S_2Na^+$ 1220.9994 $[M+Na]^+$; found 1220.9962.

2.3.6. Bis [O-2-perfluorooctylethyl-N-(phenyl)thiocarbamato] mercury(II) (**6**)

White powder; decomposes at 89 °C. IR (cm^{-1}) 1634 (ν N=C). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 2.57 (tt, 2H, $^{3}J_{H-H} = 6$ Hz, $^{3}J_{H-F} = 18$ Hz, $\underline{C}H_2-CF_2$), 4.59 (t, 2H, $^{3}J_{H-H} = 6$ Hz, CH_2-O), 6.66–7.40 (m, 5H, Ar–H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 30.51 (t, $\underline{C}H_2-CF_2$, $^{2}J_{C-F} = 22$ Hz), 60.72 (s, CH_2-O), 110.27–119.08 (m, C–F),