

Mononuclear Three-Coordinate Mercury(II)-Thiolate Complex: Synthesis and X-Ray Crystal Structure

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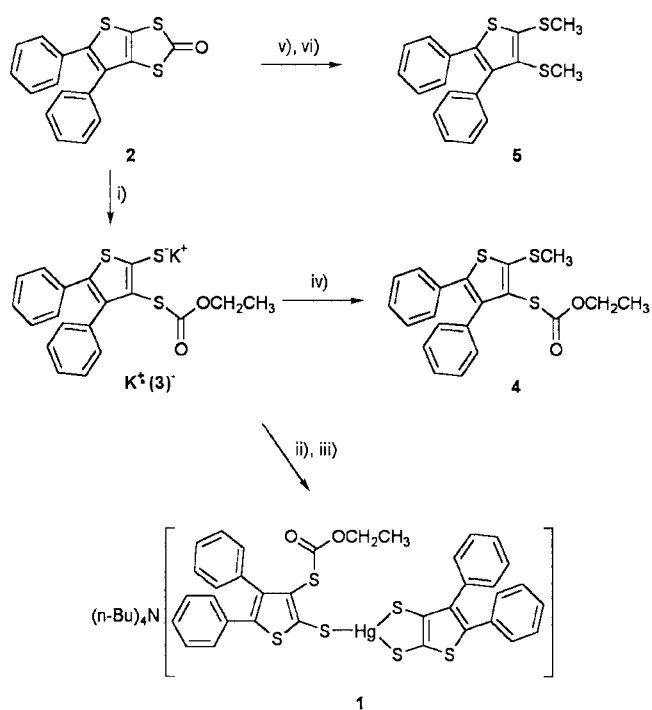
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There has been considerable interest in the complexes containing mercury(II)-thiolate bond because of their biological application¹⁻⁴ as well as their unique coordination chemistry.⁴⁻⁹ Especially in a biological system such as the MerR metalloregulatory protein, the thiolate function of a cysteine amino acid is revealed to strongly bind to mercury(II) ion in a trigonal planar geometry, which is believed to be responsible for mercury(II) detoxification.⁴ As a model compound for the mercury(II)-MerR complex, a few mononuclear mercury(II)-thiolate complexes with a trigonal planar geometry have been prepared and characterized by X-ray crystal structure analysis. Among these compounds are the tetraalkylammonium salts of $[\text{Hg}(\text{SPh})_3]^-$,⁷ $[\text{Hg}(\text{SBu}^t)_3]^-$ ⁸ and $[\text{Hg}(\text{S}-2,4,6\text{-Pr}^t_3\text{C}_6\text{H}_2)_3]^-$ ⁹ which have three equivalent monothiolate ligands, respectively. Recently, we reported an unusual dinuclear mercury(II)-thiolate complex, $[\text{Hg}_2(\text{dithiolate})_3]^-$,⁵ in which two mercury(II) ions are located in different coordination environment: one mercury(II) ion is located in a trigonal planar geometry while the other mercury(II) ion is in a highly-distorted tetragonal geometry. Here, we report the synthesis and X-ray crystal structure of the new mononuclear mercury(II)-thiolate complex of trigonal planar geometry.

The synthesis of mononuclear mercury(II)-thiolate complex **1** is outlined in Scheme 1.¹⁰ Treatment of KOH (2.0 molar ratio) to compound **2**¹¹ at room temperature results in the formation of monothiolate salt, $\text{K}^+(\mathbf{3})^-$, instead of dipotassium salt of 1,2-dithiolate. This is possibly due to the asymmetric structure of compound **2**. The formation of $\text{K}^+(\mathbf{3})^-$ was confirmed by quenching it with iodomethane and obtaining compound **4**.¹² In this compound, it can be supposed that the ethoxide moiety in ethyl thiocarbamate group comes from the solvent. Even excess amount of KOH up to 5.0 molar ratio and extended reaction time (60 min) at room temperature gave the identical monothiolate potassium salt, which was transformed to compound **4** and characterized by ¹H-NMR. When the reaction temperature, however, was raised up to 60 °C, ring-opening reaction was completely achieved and dimethyl compound **5**¹³ was obtained as yellow oil. It suggests that compound **2** can be diversely transformed to mono- and dithiolate ligand by controlling the reaction temperature. The reaction of $\text{K}^+(\mathbf{3})^-$ with HgCl_2 yielded complex **1** instead of neutral $[\text{Hg} \cdot (\mathbf{3})_2]$ complex.



Scheme 1. Reaction conditions; i) 1.7-5.0 eq. KOH/EtOH, r.t., 30 min., ii) $\text{HgCl}_2/\text{EtOH}$, iii) (n-Bu)₄NBr, iv) CH_3I , v) 5.0 eq. KOH/EtOH, 60 °C, 30 min., vi) CH_3I .

Interestingly, mono- and dithiolate ligands are incorporated together in this mercury complex. The formation of dithiolate ligand incorporated in complex **1** can be supposed to be mediated by HgCl_2 .

The molecular structure of complex **1**¹⁴ and selected interatomic parameters are presented in Figure 1. The mercury (II) ion forms distorted trigonal planar geometry with mono- and dithiolate ligands. No inter- and intra-molecular secondary interactions between mercury(II) and sulfur or oxygen are found in this complex. The central $[\text{HgS}_3]$ core is highly distorted from the regular trigonal planar geometry. The variation of the Hg-S bond distances (2.373(3)-2.495(4) Å) of the complex is significant compared to the other mononuclear three-coordinate complexes (2.407(3)-2.507(3) Å).⁷⁻⁹ The Hg-S(1) distance (2.495(4) Å) is very close to the covalent Hg-S distance (2.50 Å).⁴ The bond distances of Hg-S(2) (2.388(3) Å) and Hg-S(4) (2.373(3) Å) are relatively close to that of two-coordinate $[\text{Hg}(\text{S}-2,4,6\text{-Pr}^t_3\text{C}_6\text{H}_2)_2]$ complex (2.322(6) Å).⁹ Furthermore, the S-Hg-S angles (91.28(11)°-143.76(13)°) deviate so much from 120° obviously due to

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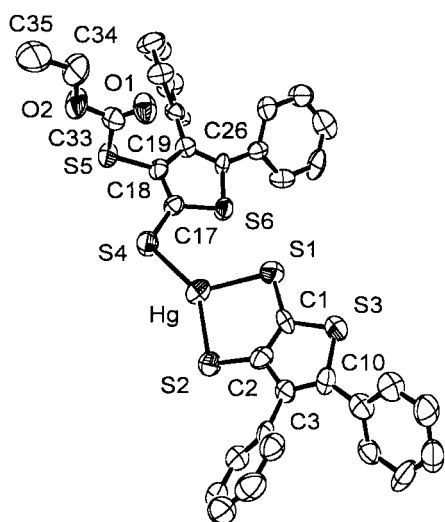


Figure 1. Molecular structure of complex **1** with ellipsoids shown at 50% probability. Hydrogen atoms and $[n\text{-Bu}_4\text{N}]$ ion are omitted for clarity. Selected bond lengths [Å] and angles [deg]: Hg-S(1) 2.495(4), Hg-S(2) 2.388(3), Hg-S(4) 2.373(3), S(1)-C(1) 1.745(12), S(2)-C(2) 1.748(13), S(3)-C(10) 1.721(13), S(3)-C(1) 1.726(12), S(4)-C(17) 1.738(12), S(5)-C(33) 1.767(15), S(5)-C(18) 1.769(12), S(6)-C(17) 1.723(12), S(6)-C(26) 1.732(12), C(1)-C(2) 1.357(15), C(2)-C(3) 1.457(15), C(3)-C(10) 1.334(16), C(17)-C(18) 1.368(14), C(18)-C(19) 1.420(15), C(19)-C(26) 1.351(15), O(1)-C(33) 1.193(15), O(2)-C(33) 1.327(16), O(2)-C(34) 1.447(17), C(34)-C(35) 1.408(19), S(4)-Hg-S(2) 143.76(13), S(4)-Hg-S(1) 124.86(12), S(2)-Hg-S(1) 91.28(11).

the chelate ligand and the relatively short Hg-S bond distances. The two thiophene moieties in complex **1** show different bond distances, which are also comparable to those of thiophene molecule (C=C: 1.37 Å; C-C: 1.42 Å)¹⁵. The difference between C-C and averaged C=C distances in thiophene moiety of the monodentate ligand (0.027 Å) is less than that of thiophene molecule (0.05 Å), while that of the chelate ligand is quite large (0.117 Å). It means that the electronic state of the thiophene moieties in the ligands is quite different from each other due to their coordination mode.

In summary, we prepared the mononuclear mercury(II)-thiolate complex of highly distorted trigonal planar geometry. Compound **2** used for ligand precursor is diversely transformed to mono- or dithiolate ligand by controlling the reaction temperature. Syntheses of several mercury(II) complexes with mono- and dithiolate ligands are under investigation.

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Supplementary Material Available. Data of crystallographic study are available on request.

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- Complex 1:** To a 30 mL ethanol suspension of **2** (1.2 mmol, 374 mg) was added KOH (2.3 mmol, 129 mg) dissolved in 20 mL ethanol under a nitrogen atmosphere, and the mixture was stirred for 30 min at room temperature. After treating HgCl₂ (0.5 mmol, 136 mg) and *n*-Bu₄NBr (1.0 mmol, 322 mg) dissolved separately in 20 mL ethanol, the yellow precipitate was filtered, washed with H₂O, ethanol and diethyl ether and dried under vacuum. The needle-shaped yellow crystals were obtained by recrystallization from acetone/ethyl acetate. Yield 79%; M.p 143-145 °C. E.A: calc. C 55.03, H 5.52, N 1.26, S 17.29% for C₅₁H₆₁HgNO₂S₆; found C 55.03 H 5.36, N 1.19, S 17.52%. ¹H NMR (500 MHz, CDCl₃) δ 7.230 (20H, Ph, m) 4.150 (2H, -OCH₂-, quartet, *J* = 7.2 Hz) 3.022 (8H, NCH₂-, m) 1.473 (8H, NCH₂CH₂-, quintet, *J* = 7.7 Hz) 1.317 (8H, N(CH₂)₂-CH₂-, sextet, *J* = 7.3 Hz) 1.196 (3H, -OCH₂CH₃, triplet, *J* = 7.2 Hz) 0.917 (12H, N(CH₂)₃CH₃, triplet, *J* = 7.4 Hz). FT-IR (KBr, cm⁻¹) 1716 (C=O) 1597, 1478 (Ar C-C) 1362 (C-N) 1138 (C-O-C) 1015 (-O-CH₂-) 880 (C-H, oop) 756, 697 (Ar C-H, oop). UV (CH₃CN, nm) 220 (s) 290 (sh) 342 (w).
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- Compound 4:** ¹H NMR (300 MHz, CDCl₃) δ 7.180 (10H, Ph, m) 4.181 (2H, -OCH₂-, quartet, *J* = 7.2 Hz) 2.580 (3H, -SCH₃, s) 1.206 (3H, -OCH₂CH₃, triplet, *J* = 7.2 Hz). FT-IR (KBr, cm⁻¹) 2988, 2921 (C-H, st) 1729 (C=O) 1138 (C-O-C).
- Compound 5:** ¹H NMR (300 MHz, CDCl₃) δ 7.186 (10H, Ph, m) 2.508 (6H, -SCH₃, s). FT-IR (KBr, cm⁻¹) 2936, 2919 (C-H, st).
- Crystal data for 1:* C₅₁H₆₁HgNO₂S₆, Mr=1112.96, monoclinic, space group P2(1)/a, *a*=18.646(3), *b*=15.043(3), *c*=20.151(3) Å, β = 116.090(10)°, *U* = 5076.3(15) Å³, *Z* = 4, *D*_c=1.456 Mg/m³, *F*(000)=2264, μ(Mo-Kα)=3.317 mm⁻¹, Crystal size=0.17 × 0.20 × 0.35 mm³, *R*(*R*_w)=0.0552(0.0827) [*I*>2σ(*I*)]. Data were collected on an Enraf-Nonius CAD-4 automatic diffractometer at 293(2)K.
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