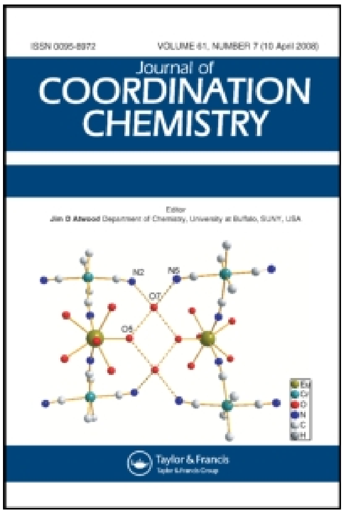

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Synthesis and crystal structure of bis{(μ-chloro)-chloro-[N-benzoyl-N′-(2-hydroxyethyl)thiourea] mercury(II)}

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The complex bis{(μ-chloro)-chloro-[N-benzoyl-N′-(2-hydroxyethyl)thiourea] mercury(II)} was prepared by reaction of $HgCl_2$ with N-benzoyl-N′-(2-hydroxyethyl) thiourea(HL). The compound was characterized by IR and ^1H NMR spectroscopy and its structure was determined by single crystal X-ray diffraction. The complex is binuclear with two Hg(II) ions tetrahedrally coordinated by a terminal chloride, two bridging chlorides and a HL molecule. The Hg(II) ion is coordinated with HL via S(1).

Keywords: Mercury(II) complexes; Chloro-bridged complexes; N-benzoyl-N′-(2-hydroxyethyl)-thiourea ligand

1. Introduction

Mercuric ion is highly toxic to many organisms and research for new ligands with enhanced affinity for toxic metals has attracted much interest [1–5]. In recent years, owing to their strong coordination ability with transition metal ions, many N-substituted N′-alkoxycarbonyl thioureas have been extensively utilized as sequestering agents for copper sulfides and other precious metals [6]. In view of these and as a part of our research on coordination complexes of thiourea derivatives [7–11], we synthesized a series of thiourea derivatives and their mercury (II) complexes. In the present article, we report the reactions of the N-benzoyl-N′-(2-hydroxyethyl)thiourea [HL] with Hg(II) and the crystal structure of the title complex.

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2. Experimental

2.1. *Synthesis*

The N-benzoyl-N′-(2-hydroxyethyl)thiourea was prepared according to our previous work [7]. To an ethanol (30 cm^3) solution of the ligand (2 mmol, 0.448 g) mercury(II) chloride (2 mmol, 0.453 g) was added under constant stirring. After stirring the reaction mixture at room temperature for 2 h, the mixture was filtered to obtain white solid, which was dried in air and recrystallized from ethanol. Single crystals of the title compound were obtained after one week by slow evaporation of the ethanol solution.

2.2. *Physical measurement*

Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN instrument. Anal. Calcd for $C_{20}H_{24}N_4O_4S_2Hg_2Cl_4$(%): C, 24.14; H, 2.33; N, 5.39; Found: C, 24.40; H, 1.98; N, 5.41. The infrared spectrum was recorded on a Nicolet NEXUS 670 IR spectrophotometer using KBr discs. ^{1}H NMR spectra were recorded on an Avanced 300 Bruker spectrometer with DMSO-d_6 as solvent and TMS as an internal reference.

2.3. *Crystal structure determination*

Intensity data of the title compound were collected at 293(2) K on a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation, using the φ–ω scan mode. Data collection and reduction were performed using SMART and SAINT software [12]. An empirical absorption correction was applied to the raw intensities by using SADABS [13]. The structure was solved by direct methods and full-matrix least-squares based on F^2 using the SHELXTL program package [14]. Non-hydrogen atoms were subjected to anisotropic refinement. Selected crystal data and structure refinement details are presented in table 1.

3. Results and discussion

3.1. *Crystal structure*

The molecular structure of the title compound is shown in figure 1. Selected bond distances and angles are listed in table 2. The molecule is a dimeric complex, the halves being related by the centre of symmetry. Each Hg atom is bound to two bridging chlorine atoms [distances: 2.396(3) and 2.914(2) Å for Hg(1)–Cl(2) and Hg(1)–Cl(2A), respectively], one terminal chlorine atom [Hg(1)–Cl(1), 2.491(2) Å] and one sulfur atom from the ligand [Hg(1)–S(1); 2.431(3) Å]. The two Hg and the two bridging Cl atoms are in a nearly square-planar arrangement [angles: 86.63(8) and 93.37(8)° for Cl(2A)–Hg(1)–Cl(2) and Hg(1)–Cl(2)–Hg(1A), respectively]. The four atoms [Hg(1), Hg(1A), Cl(2), Cl(2A)] are exactly in the same plane; the mean deviation from plane is 0.000 Å. The wide Cl(2)–Hg(1)–S(1) angle of 135.96(9)° is intermediate between linear and trigonal geometry, suggesting that the preferred linear coordination of the strongly bonding Cl(2) and S(1) about mercury(II) is severely distorted by the presence of the weakly coordinated Cl(1). The C=S bond distance is sensitive to coordination;

Table 1. Crystal data and structure refinement details for $Hg_2(HL)_2Cl_4$.

Formula	$C_{20}H_{24}N_4O_4S_2Hg_2Cl_4$
Formula weight	991.546
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	7.3497
b (Å)	8.0356
c (Å)	11.8556
α (°)	77.812
β (°)	81.932
γ (°)	83.145
V (Å^3)	674.71(4)
Z	4
D_{Calcd} (g cm^{-3})	2.440
Absorption correction	Empirical
$F(000)$	464
Limiting indices	$-6 \le h \le 8$, $-9 \le k \le 9$, $-14 \le l \le 14$
θ range (°)	1.77–25.27
Reflections collected	3996
Independent reflections	2396 [$R(\text{int}) = 0.0559$]
Data/restraints/parameters	2396/0/164
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0522$, $wR_2 = 0.1353$
R indices (all data)	$R_1 = 0.0558$, $wR_2 = 0.1395$
Goodness of fit on F^2	1.088
Extinction coefficient	0.024(2)
Largest diff. peak and hole (e Å^{-3})	1.706, −2.266

MERCURY(II) AND THIOUREA DERIVATIVES

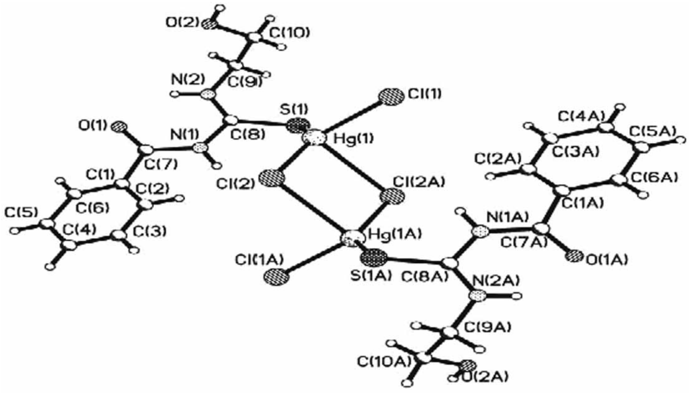

Figure 1. The molecular structure of title complex, the 50% probability of the thermal ellipsoids.

the C=S bond distance of 1.707(8) Å is longer than the C=S bond length of 1.663(8) Å in the free ligand. This longer C=S distance arises from the strong coordination of the thiocarbonyl sulfur to soft mercury(II) which weakens the C(8)=S(1) bond.

3.2. *Spectroscopic data*

The IR spectrum of the title complex shows two bands at 3412.6 and 3154.0 cm^{-1} due to N–H stretching vibration. A strong band at 1183.4 cm^{-1} is assigned as the thionyl group, which has a 51.6 cm^{-1} red shift compared with 1235.0 cm^{-1} in free thiourea, indicating coordination of the thionyl group with mercury(II).

Table 2. Selected bond distances (Å) and bond angles (°) for the complex.

Hg(1)–Cl(2)	2.396(3)	N(2)–C(8)	1.287(12)
Hg(1)–Cl(1)	2.491(2)	N(2)–C(9)	1.452(12)
Hg(1)–S(1)	2.431(3)	O(1)–C(7)	1.207(11)
Hg(1)–Cl(2A)	2.914(2)	O(2)–C(10)	1.419(11)
Cl(2)–Hg(1A)	2.914(2)	N(1)–C(7)	1.379(12)
S(1)–C(8)	1.707(8)	N(1)–C(8)	1.376(12)
Cl(2)–Hg(1)–S(1)	135.36(9)	C(8)–S(1)–Hg(1)	99.9(3)
Cl(2)–Hg(1)–Cl(1)	114.64(9)	C(7)–N(1)–C(8)	126.7(7)
S(1)–Hg(1)–Cl(1)	90.89(8)	C(8)–N(2)–C(9)	124.4(8)
Cl(2)–Hg(1)–Cl(2A)	86.63(8)	O(1)–C(7)–N(1)	122.3(8)
S(1)–Hg(1)–Cl(2A)	96.63(8)	N(1)–C(7)–C(1)	115.4(7)
Cl(1)–Hg(1)–Cl(2A)	89.87(8)	N(2)–C(8)–S(1)	122.9(7)
Hg(1)–Cl(2)–Hg(1A)	93.37(8)	N(2)–C(9)–C(10)	113.4(8)
N(2)–C(8)–N(1)	119.5(8)	O(2)–C(10)–C(9)	110.2(7)
N(1)–C(8)–S(1)	117.4(6)		

Symmetry transformations used to generate equivalent atoms: #1: $-x+1$, $-y+1$, $-z+1$.

^{1}H NMR data [$\delta = 3.69$ (4H, t, CH_3) $\delta = 3.63$ (4H, t, CH_2) $\delta = 5.40$ (2H, s, OH) $\delta = 7.56 \sim 7.96$ (4H, m, Ar–H) and $\delta = 11.41$ (4H, s, NH)] are consistent with the structure of title compound.

4. Conclusions

Research about N-benzoyl-N′-(2-hydroxyethyl)thiourea had been reported by Koch, *et al.* [15] in 1995. In the article, the molecular structure of $Pt(HL)_2Cl_2$ was studied by ^{1}H NMR and (+)FAB mass spectrum. The result shows that HL behaves like a monodentate thiourea ligand and reacts with Pt(II) to yield a mixture of cis and trans complexes. Furthermore, in our previous work [11], desulphurization and cyclization were found and the oxazoline ring was formed in the reaction of N-benzoyl-N′-(2-hydroxyethyl)thiourea with $CuCl_2$. In this article, the title complex was prepared by the reaction of $HgCl_2$ with HL. The molecular structures of these complexes were quite different in these works. As a result, metal ions play an important role in the reaction of the ligand.

Supplementary material

Crystallographic data for the structure reported in this article have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 251030. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union road, Cambridge CB21EZ, UK(fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgments

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