The synthesis, structure and magnetic properties of a mononuclear cobalt compound with dipyrimidine sulfane ligand derived from 2-thio-barbituric acid

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ARTICLE INFO

ABSTRACT

A new mononuclear compound named triaqua-(2,2′-di-thio-4,6,4′,6′-tetraoxo-5,5′-dipyrimidine-sulfanediyl-κ^3O,O',S)-cobalt(II) (**1**) was prepared by the solvothermal reaction of 2-thio-barbituric acid (TBA), $CoCl_2$ and KOH in ethanol–water mixed solution. The supposed probable reaction mechanism shows that TBA desulfur coupling into 5,5′-dipyrimidine-sulfane is the key process of forming **1**. Variable-temperature magnetic susceptibilities display intermolecular antiferromagnetic interactions in **1**.

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1. Introduction

2-Thio-barbituric acid (TBA for short) is a kind of pyrimidine derivative, and has two structural types: ketone form (4,6-dioxo-2-thio-pyrimidine) and enol form (4,6-dihydroxy-2-mercapto-pyrimidine). The ketone form is the advantage type (Scheme 1). The main application of TBA is the TBA test for the measurement of lipid oxidation, which has been discovered over 60 years before [1]. From then on, the TBA test has been widely used for the measurement of the oxidative state of biological and food materials [2–8]. Surprisingly, the TBA coordinated metal complexes have been scarcely reported [9–11], perhaps as the reason of its unstability. TBA can easily hydrolyze and be oxidized under concentrated acid or high temperature [12]. In this paper, a cobalt compound **1** (Scheme 1) was obtained when TBA reacted with $CoCl_2$ and KOH in ethanol–water under solvothermal reaction conditions. It is supposed that TBA desulfur coupling into 5,5′-dipyrimidine-sulfane is the key process to form the final mononuclear complex **1**. The probable reaction mechanism and the magnetic properties of **1** have been carefully studied.

2. Experimental

### 2.1. Materials and physical methods

All reagents were of A.R. grade and used without further purification. Elemental analyses for C, H, N and S were performed on a Vario EL III elemental analyzer. Diffraction studies on single crystal was conducted on a Bruker SMART APEX II CCD diffractometer applying graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Variable-temperature magnetic susceptibility measurements were performed on a MPMS Multivu device. All data were collected at room temperature except for magnetic measurement.

2.2. Synthesis of triaqua-(2,2′-di-thio-4,6,4′,6′-tetraoxo-5,5′-dipyrimidine-sulfanediyl-κ^3O,O',S)-cobalt(II) (**1**)

$CoCl_2 \cdot 6H_2O$ (0.5 mmol, 0.119 g) and 2-thio-barbituric acid (TBA, 1.0 mmol, 0.145 g) were dissolved in 20 ml of ethanol–H_2O (v/v, 1:1) and then the pH of the obtained mixture was adjusted with KOH (0.5 mol/L) to pH = 8.0. After that, the mixed solution was sealed in a 25 mL Teflon reactor and kept under autogeneous pressure at 130 °C for 5 days. After cooling to room temperature at a rate of 6°Ch^{-1}, red block shaped crystals suitable for X-ray diffraction were grown from the filtrate by slow evaporation. Yield: 103 mg (48% based on Co). *Anal.* Calc. for $C_8H_{10}CoN_4O_7S_3$: C,

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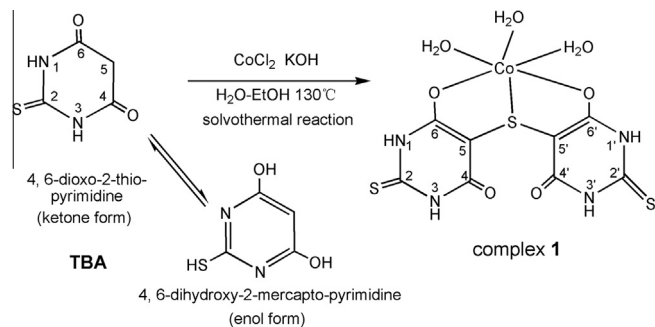
Scheme 1. The ketone form and enol form of TBA together with the preparation method of **1**.

22.36; H, 2.33; N, 13.04; S, 22.36. Found: C, 22.30; H, 2.26; N, 13.12; S, 22.41%.

2.3. X-ray crystallographic studies

Single crystal suitable for X-ray diffraction analysis of complex **1** was carried out. Red crystal of **1** was put on a Bruker SMART APEX II CCD diffractometer and X-ray diffraction intensities were measured by using the $\theta - 2\omega$ scan technique at room temperature. The structures was solved by direct methods [13,14] and refined by full-matrix least squares on F^2 using the SHELXL97 software [15]. All the non-hydrogen atoms were refined anisotropically. The N–H hydrogen atoms were refined in calculated positions using the riding model approximation, their isotropic temperature factors in the least-squares refinements is −1.5. The O–H hydrogen atoms were located from difference Fourier maps. The crystallographic data of **1** are shown in Table 1.

3. Results and discussion

3.1. Structure description for complex **1**

The single crystal X-ray diffraction studies revealed that compound **1** is a mononuclear complex and the asymmetric unit is comprised of one Co^{II} ion, one 2,2′-di-thio-4,6,4′,6′-tetraoxo-5,5′-dipyrimidine sulfanediyl dianion (L^{2-} for short) and three water ligands. The Co^{II} ion is located in an elongated SO_5 octahedral

Table 1
Crystallographic data for compound **1**.

Compound	**1**
Empirical formula	$C_8H_{10}CoN_4O_7S_3$
Formula weight	429.31
T (K)	296(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	15.3845(15)
b (Å)	15.7923(16)
c (Å)	14.1218(14)
α (°)	90
β (°)	93.7400(10)
γ (°)	90
V (Å³)	3423.7(6)
Z	8
D_{calc} (Mg m^{-3})	1.666
Crystal size (mm)	0.47 × 0.17 × 0.09
Reflections collected	12 549
Independent reflections (R_{int})	3192(0.0197)
R indices ($I > 2\sigma(I)$)	$R_1 = 0.0286$, $wR_2 = 0.0846$
R indices (all data)	$R_1 = 0.0311$, $wR_2 = 0.0863$

$w(\mathbf{1}) = 1/[\sigma^2(F_o)^2 + (0.0524P)^2 + 3.0733P]$, $P = (F_o^2 + 2F_c^2)/3$.
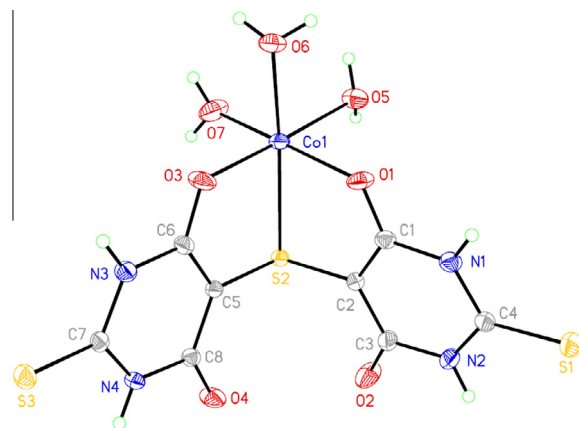
Fig. 1. The molecular structure of **1**, showing the atom-numbering scheme. Thermal ellipsoids are shown at 30% probability level.

environment formed by three water molecules and one L^{2-} ligand (Co1–O5 = 2.089(2) Å, Co1–O6 = 2.136(1) Å, Co1–O7 = 2.064 (1) Å, Co1–O3 = 2.037(2) Å, Co1–O1 = 2.088(2) Å, Co1–S2 = 2.519(6) Å) (Fig. 1). The O1, O3, O7, O5 atoms define the equatorial plane and O6, S2 atoms occupy the axial positions. Co1 deviates from the equatorial least-squares plane O1/O3/O7/O5 by 0.0014 Å toward S2, with the O6–Co1–S2 angle of 169.44(5)°. L^{2-} binds to the Co^{II} center in the tridentate chelate mode forming two five-membered chelate Co–O–C–C–S rings. The dihedral angle between the least-squares plane of the two chelate rings is 82.49°.

The coordinated H_2O ligands as hydrogen donors are involved in intermolecular hydrogen bonding interactions with free oxygen and free sulfur atoms of L^{2-} as acceptors (Table 2). Adjacent mononuclear units of **1** are stabilized and constructed into a three dimensional network by these O–H···O hydrogen bonds (Fig. 2).

3.2. Probable synthesis mechanism for complex **1**

Based on the crystal structure of complex **1**, a probable reaction mechanism for obtaining **1** from TBA, $CoCl_2$ and KOH under solvothermal reaction condition has been proposed (Scheme 2). It has been known that ketone form of TBA is the main structural type; the 5-methylene group is very active and 5-carbon atom has some positive electrical properties [12]. At first, the TBA occurs desulfur reaction, and forms barbituric acid and H_2S under high temperature [12]. Then, H_2S is neutralized by KOH and S^{2-} is formed. After that, S^{2-} attacks the 5-carbon atom of TBA in the alkaline medium, and 2,5-di-thio-barbiturato anion species is obtained. At the same time, trace amount of S^{2-} (3%) also reacts $CoCl_2$ to form little CoS precipitates. In the next step, this anion attacks the 5-carbon atom of another TBA forming a new coupling molecule: 2,2′-di-thio-4,6,4′,6′-tetraoxo-5,5′-dipyrimidine-sulfane. Similarly, this sulfane also has tautomeric equilibrium

Table 2
Hydrogen bonds geometries (Å, °) for compound **1**.

Donor–H···acceptor	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(6)–H(4W)···O(2)[a]	0.82	2.03	2.794(3)	154
O(7)–H(6W)···O(2)[a]	0.82	1.84	2.641(3)	164
O(7)–H(5W)···S(3)[b]	0.83	2.50	3.297(2)	162
O(5)–H(2W)···O(4)[a]	0.83	1.94	2.760(2)	171
O(5)–H(1W)···S(1)[c]	0.82	2.38	3.174(2)	164

Symmetry codes.
[a] $-x + 1/2$, $y - 1/2$, $-z + 1/2$.
[b] $-x$, y, $-z + 1/2$.
[c] x, $-y + 1$, $z + 1/2$.