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Synthesis, Structure and Properties of Tetrakis (thiourea) mercury (II) Tetrakis (thiocyanato-N) zinc (II)

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Abstract: A new nonlinear optical complex crystal tetrakis (thiourea) mercury (II) tetrakis (thiocyanato-N) zinc (II) was synthesized and its structure was determined. It belongs to the tetragonal system, $I\bar{4}$ space group. The crystal structure consists of discrete $[Zn(SCN)_4]^{2-}$ anions and $[Hg(NH_2CSNH_2)_4]^{2+}$ cations with slightly distorted coordination tetrahedra ZnN_4 and HgS_4. The second harmonic generation (SHG) of the crystal was found to be superior to that of urea.

Keywords: TMTZ crystal, synthesis, structure, properties.

Introduction

In recent years, much attention has been paid to the research of novel, high-quality nonlinear optical (NLO) crystals, especially those metalorganic complex crystals that can generate high efficient second-harmonic blue-violet light using GaAlAs laser diodes. In order to find this type of crystals, much work has been done in our laboratory on the complex crystals of $MM'(SCN)_4$ and MM'(SCN) • nL, where M = Zn, Cd, Mn; M' = Cd, Hg and L = adduct[1-6]. A 404.5nm blue-violet light output of 1.8 mW by frequency doubling of a 809nm GaAlAs laser diode using a cadmium mercury thiocyanate crystal ($CdHg(SCN)_4$) has been realized at room temperature[2], which shows great potential application of this type of complex crystals. As part of continuous work, we report here the synthesis, structure and properties of a new complex crystal tetrakis (thiourea) mercury (II) tetrakis (thiocyanato-N) zinc (II), $[Hg(NH_2CSNH_2)_4]^{2+}[Zn(SCN)_4]^{2-}$ (abbreviated as TMTZ).

Synthesis

The title compound could be synthesized by two methods. One method is: 0.4 mol KSCN was dissolved in 200 ml distilled water and then 0.1 mol $HgCl_2$ powder was added. With stirring, the $HgCl_2$ powder dissolved quickly, and the mixture solution I was obtained. Then 0.1 mol $ZnCl_2$ and 0.4 mol thiourea was dissolved in ml distilled water (solution Ⅱ). Solution I and II were heated to 40℃ then mixed, forming

solution III. The other method was performed in two steps. First, synthesis of ZnHg(SCN) (ZMTC) : following the above mentioned steps, the solution I′ was obtained with 0.8 mol KSCN and 0.2 mol $HgCl_2$, and then solution II′ of 0.2 mol $ZnCl_2$ in 100 ml water was added into solution I′ at room temperature. The white precipitate of ZMTC was filtered, washed with distilled water and dried at 30°C; Second, dissolve the ZMTC powder into 200 ml solution of 0.1 mol thiourea at 40°C. Keep stirring until the solution got supersaturated (solution III′). It was found that 12.65 g ZMTC powder was dissolved in solution III′ . Both solution III and solution III′ were kept at 40°C. The transparent needle-like single crystals were obtained by evaporation of solvent for one day. Calcd. for TMTZ: C, 11.97%; H, 2.01%; N, 20.94%. Found (obtained by method one) C, 11.92%; H, 1.98%; N, 20.97%. Found (obtained by method two): C, 11.89%; H, 1.97%; N, 20.91%.

Structure

A transparent single crystal of the title compound obtained by method one with dimension of 0.20× 0.25×0.26 mm^3 was used to determine its structure by a R3m/E four-circle X-ray diffractometer. It belongs to tetragonal system, $I\bar{4}$ space group with parameters a = 17.2772(8) Å, c=4.2636(5) Å, Z = 2, Dc = 2.095 g/cm^3, R = 0.0367, and Rw = 0.0936. The crystal structure of TMTZ consists of discrete $[Zn(NCS)_4]^{2-}$ anions and $[Hg(NH_2CSNH_2)_4]^{2+}$ cations (**Figure 1**).

Table 1 The bond parameters of TMTZ

Bonds and angles	Zn-N	Hg-S	N-Zn-N'	S-Hg-S'	C-N In SCN^-	S-C in SCN^-
Parameters (Å, °)	1.963 (10)	2.5706 (17)	118.6(6) 105.1(3)	113.88(6) 107.31(5)	1.170(12)	1.618(7)

It can be seen from the bonds and angles (**Table 1**) and crystal structure (**Figure 2**) that the corresponding tetrahedra ZnN_4 and HgS_4 are slightly flattened along the Z axis with a local symmetry of D2d and the ZnN_4 tetrahedra are distorted more severely than the HgS_4 tetrahedra. The central atoms, Zn and Hg, are just located at the fourfold inversion axis of the flattened tetrahedra. The C1-N1 bond distance of SCN^- is slightly longer than the normal triple-bond length of 1.15 Å, while the S1-C1 bond distance is shorter than the normal single bond of 1.81 Å. It is because that when thiocyanate ion binds with Zn through N atom, the C ≡ N is weakened while the S-C single bond is strengthened due to the electron drift towards the N atom [7].

Properties

The second-order intensity nonlinear optical tests of the crystal were carried out by the powder second harmonic generation (SHG) method[8]. Irradiated by a 1064nm passive mode-locked Nd:YAG laser beam, the TMTZ crystal showed a 532nm second harmonic that is much superior to that of urea. The DSC and TG of TMTZ crystal were carried

out. The result showed that the crystal underwent two steps of decomposition from the temperature 450.4K to 864.8K, which was followed by melting.

Figure 1 Molecular structure of TMTZ containing discrete $[Zn(NCS)_4]^{2-}$ anions and $[Hg(NH_2CSNH_2)_4]^{2+}$ cations

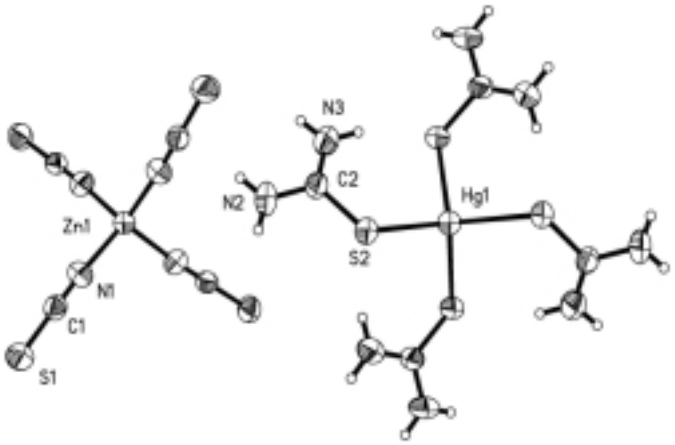
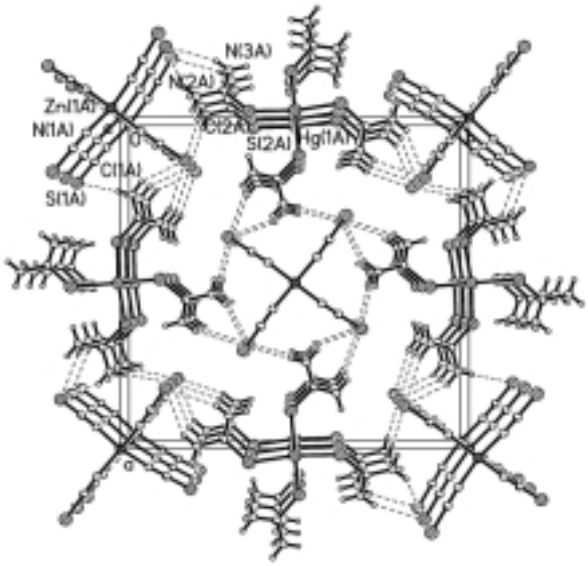


Figure 2 The projection of unit cell of TMTZ along c direction



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