Crystal structure of crystal structure of tetrakis(thiourea)cadmium tetrakis(thiocyanato)zincate, $[\text{Cd}(\text{NH}_2\text{CSNH}_2)_4][\text{Zn}(\text{SCN})_4]$

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Abstract

$\text{C}_8\text{H}_{16}\text{CdN}_{12}\text{S}_8\text{Zn}$, tetragonal, $\bar{4}$ (No. 82), $a = 17.258(2)$ Å, $c = 4.2647(7)$ Å, $V = 1270.1$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.069$, $wR_{\text{ref}}(F^2) = 0.186$, $T = 293$ K.

Source of material

The title compound was synthesized by the reaction of zinc chloride, cadmium chloride, potassium thiocyanate and thiourea in stoichiometric amounts at about 313 K in water. The mother solution after synthesis was kept at 323 K for one day and the transparent single crystals were obtained.

Discussion

In recent years, much attention has been paid to the research of novel, high-quality nonlinear optical (NLO) crystals, especially those metalorganic or semiorganic complex crystals, which combine the advantages of inorganic crystals, such as good stability, with the advantages of organic crystals, such as high nonlinearity, and 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 on the complex crystals of $\text{MM}'(\text{SCN})_4$ and $\text{MM}'(\text{SCN})_4 \cdot n\text{L}$, where $\text{M} = \text{Zn}, \text{Cd}, \text{Mn}$; $\text{M}' = \text{Cd}, \text{Hg}$ and $\text{L} = \text{adducts}$ [1–10]. The synthesis, crystal structure and properties of zinc cadmium thiocyanate (ZCTC) has been reported [2, 6]. As part of continuous work, we report here the structure and properties of tetrakis(thiourea)cadmium tetrakis(thiocyanato)zincate (TCTZ).

Thiocyanate ions can bind to metal ions through either S or N. Thiourea (NH_2CSNH_2 , tu) is also a bidentate ligand with a sulphur or nitrogen as potential electron donor. According to the Hard and Soft Acids and Bases (HSAN) concept [11], the different types of binding to SCN or thiourea depend on the hardness of metal ions. Therefore, the hard Zn binds through the hard N atom while Cd can bind through either N or S atoms because the hardness of Cd is just between the hard Zn and soft Hg. In the crystal TCTZ, the Zn ions are surrounded tetrahedrally by four N atoms of the thiocyanates, with a Zn—N bond distance of 2.0242 Å and angles of 107.18° and 114.15°, while the Cd ions are surrounded by four S atoms of the thiourea ligands, with a Cd—S bond distance of 2.5702 Å and angles of 107.35° and 113.81°, forming separated $[\text{Zn}(\text{NCS})_4]^{2-}$ and $[\text{Cd}(\text{NH}_2\text{CSNH}_2)_4]^{2+}$ tetrahedral structures, respectively. In ZCTC, however, the $-\text{S}=\text{C}=\text{N}-$ act as bridges linking ZnN_4 and CdS_4 tetrahedra into infinite three-dimensional network. The C1—N1 and S1—C1 bond distances (1.0722 Å and 1.6506 Å, respectively) are slightly shorter than those in ZCTC (1.153(6) Å and 1.651(5) Å, respectively), because SCN^- acts as monodentate ligand through N atom in TCTZ while as bidentate ligand in ZCTC. From the bonds and angles, it is obvious that the structure of $\text{ZCTC} \cdot 4\text{tu}$ consists of slightly flattened $[\text{Zn}(\text{NCS})_4]^{2-}$ and $[\text{Cd}(\text{NH}_2\text{CSNH}_2)_4]^{2+}$ tetrahedral units, which are connected by the hydrogen bonds between the H atoms of the thioureas and the S atoms of the neighboring thiocyanates, forming three-dimensional framework. The central Zn and Cd atoms of the tetrahedra are located on 4 inversion point. The macroscopic nonlinear susceptibility of TCTZ may be related to the microscopic hyperpolarisabilities of the dipolar thiocyanate ions and the distorted tetrahedra. The second harmonic generation (SHG) effect of the crystal was determined. It was found that the TCTZ crystal is comparable with ZCTC crystal in the SHG effects.

Table 1. Data collection and handling.

Crystal:	colourless needle, size 0.15 × 0.18 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ :	24.62 cm ⁻¹
Diffraction, scan mode:	Bruker P4, $\theta/2\theta$
$2\theta_{\text{max}}$:	60°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	1445, 1339
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1259
$N(\text{param})_{\text{refined}}$:	69
Program:	SHELXTL [12]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	Occ.	x	y	z	<i>U</i> _{iso}
H(3A)	8g		0.1329(8)	0.3684(9)	0.283(6)	0.113
H(3B)	8g		0.2172(8)	0.3559(9)	0.229(6)	0.113
N(2')	8g	0.4(2)	0.264(2)	0.470(2)	0.55(2)	0.05(1)
H(2'A)	8g	0.4	0.302(2)	0.438(2)	0.54(2)	0.064

Table 2. Continued.

Atom	Site	Occ.	x	y	z	<i>U</i> _{iso}
H(2'B)	8g	0.4	0.271(2)	0.515(2)	0.63(2)	0.064
N(2)	8g	0.6	0.268(2)	0.473(2)	0.44(2)	0.070(9)
H(2A)	8g	0.6	0.304(2)	0.444(2)	0.37(2)	0.084
H(2B)	8g	0.6	0.280(2)	0.516(2)	0.53(2)	0.084

Table 3. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cd(1)	2c	0	1/2	1/4	0.0271(4)	<i>U</i> ₁₁	0.0473(7)	0	0	0
Zn(1)	2a	0	0	0	0.057(1)	<i>U</i> ₁₁	0.093(2)	0	0	0
C(1)	8g	0.1231(9)	0.0926(9)	0.370(5)	0.064(7)	0.058(6)	0.10(1)	0.005(6)	0.002(7)	0.006(7)
C(2)	8g	0.1951(8)	0.4504(9)	0.430(4)	0.051(6)	0.067(7)	0.09(1)	0.005(5)	0.005(6)	0.015(7)
N(1)	8g	0.0772(7)	0.0608(6)	0.260(7)	0.067(5)	0.062(5)	0.095(8)	0.010(4)	0.01(1)	0.00(1)
N(3)	8g	0.1801(8)	0.3841(9)	0.299(6)	0.062(6)	0.081(7)	0.14(2)	0.010(5)	0.01(1)	0.04(1)

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