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A Novel Nonlinear Optical Complex Crystal with an Organic Ligand Coordinated through an O Atom: Tetrathiocyanatocadmiummercury-Dimethyl Sulfoxide

A novel nonlinear optical complex crystal with an organic ligand coordinated through an O atom: tetrathiocyanatocadmiummercury-dimethyl sulfoxide, $[CdHg(SCN)_4(H_6C_2OS)_2]$, (CMTD) is reported for the first time. Single crystals have been grown by temperature-lowering method, the crystal structure has been determined, and some physical properties are given. The relations between the crystal structure and nonlinear optical properties are also discussed.

Keywords: nonlinear optical complex crystal, organic ligand

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1. Introduction

In the last decade, nonlinear optical (NLO) crystals have attracted much attention because of their potential applications in many fields. Though organic NLO crystals have high nonlinearity, fast response and tailor-made flexibility, their applications were limited due to their shortcomings, such as poor chemical stability, poor phase matching caused by a large birefringence, red-shift of the cut-off wavelength caused by a large organic π-conjugated system, etc.

In order to solve these problems, the research of our group aimed at the complex crystal family, and in 1987, the double radical structure model theory was proposed for the first time (XU et al.). Under the guiding of this theory many new organometallic complex crystals, such as BTCC (XING et al.), TSCCC (TAO et al.), ATCC (ZHANG et al.), ATCB (YUAN et al. 1990), ATMC (YUAN et al. 1991), CMTC (YUAN et al. 1997), ATMB (HOU et al.) et al., have been found and synthesized, all of them have good NLO properties. The NLO crystal of cadmium mercury thiocyanate (CMTC), which may be generate second harmonic blue--violet light by using GaAlAs laser diode, has been reported by us (Yuan et al. 1997). In this paper we report a novel nonlinear optical complex crystal, tetrathiocyanatocadmiummercury-dimethyl sulfoxide (CMTD), $[CdHg(SCN)_4(H_6C_2OS)_2]_n$, large single crystals of which have been grown by temperature-lowing method from aqueous solution. Systematic studies of these crystals have been carried out and will be reported continually. Crystal structure and some physical properties are reported in this paper and the relations between the crystal structure and NLO properties are also discussed.

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2. Experimental

2.1 Crystal growth

Small single crystals can be obtained by spontaneous nucleation in the solution made by CMTC as raw materials in a 3:1 mixture of dimethyl sulfoxide (analytical trade reagent) and de-ionized water. A small single crystal without macrodefects was selected as seed so that the crystal can be grown fast in good quality. The growth temperature was decreased from 43 to 22°C. Within 45 days, a colorless, high optical quality single crystal with size 25×23×15 mm^3 could be obtained.

Table 1: Crystal data, detail data collection, structure analysis and refinement

Empirical Formula	C8 H12 Cd Hg N4 O2 S6
Formula Weight	701.64
Crystal System	Orthorhombic
Space group	P212121 (No. 19)
a, b, c [Angstrom]	8.5188(6), 8.5398(7), 28.224(6)
alpha, beta, gamma [deg]	90, 90, 90
V [Ang**3]	2053.3(5)
Z	4
D(obs), D(calc) [g/cm**3]	0.000, 2.270
F(000)	1312
Mu(MoKa) [/mm]	9.1
Crystal Size [mm]	0.00 x 0.00 x 0.00
Data Collection	
Temperature (K)	293
Radiation [Angstrom]	MoKa, 0.71073
Theta Min-Max [Deg]	2.5, 25.0
Scan,(Type & Range) [Deg]	0.00 + 0.35 Tan(Theta)
Hor. and vert. aperture [mm]	0.00, 0.00
Reference Reflection(s)	
Dataset	-1: 9 ; -1: 10 ; -33: 1
Tot., Uniq. Data, R(int)	2745, 2532, 0.072
Observed data [I > 2.0 sigma(I)]	1920
Refinement	
Nref, Npar	2532, 200
R, wR, S	0.0467, 0.1428, 1.10
w = 1/[\s^2^(Fo^2^)+(0.0756P)^2^+2.5713P] where P=(Fo^2^+2Fc^2^)/3	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. dens. [e/Ang^3]	-0.88, 1.26

2.2 Crystal structure determination

The crystal structure was determined for the first time by a four-circle diffractometer (Bruker P4). Table 1 shows the crystallographic data of CMTD; Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-hydrogen atoms are also given in table 2.

The results show that CMTD belongs to the orthorhombic system, space group $P2_12_12_1$ and point group 222. The unit cell parameters: a= 8.5188(6) Å, b=8.5398(7) Å, c=28.224(6) Å, V=2053.3(5) $Å^3$, Z=4 and Dm=2.270 g/cm^3. The molecular structure is shown in fig. 1.

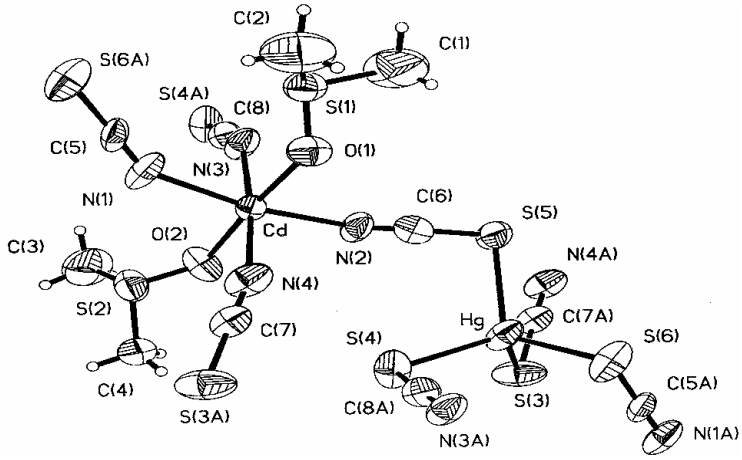

Fig. 1: The molecular structure of CMTD crystal

Thiocyanate (SCN^-) bind to metal ions by either S or N atom. Hg^{2+}, as a center ion, connect to four SCN ligands by S, which forms a slightly distorted tetrahedron; Cd^{2+}connect to four NCS ligands by N and connect to two DMSO ligands by O forms a slightly distorted octahedron. The —SCN— bridge connects Hg and Cd forming infinite three--dimensional —Cd—SCN—Hg— networks. This packing structure feature donates high nonlinear optical property, physical and chemical characterized to CMTD crystal.

The bond angle and the bond length data are listed in table 3.

2.3 Physical properties

Preliminary results show that the efficiency of CMTD crystal powder SHG is 15 times of urea and is larger than that of CMTC crystal.

The transmission curve of CMTD crystal measured by a Hitachi model U-3500 spectrophotometer is shown in fig. 2.

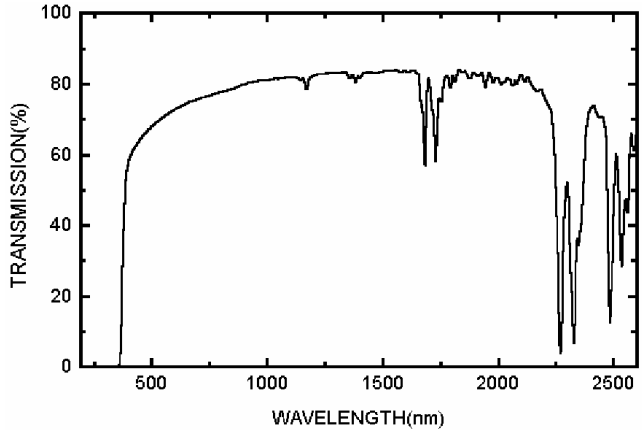

Fig. 2: The transmission curve of CMTD crystal

Light beam was incident along the [001] direction (thickness 2.3 mm). The crystal is transparent from 0.36 μm to 2.26 μm, the violet-shift is 18 nm compared with CMTC crystal, which was reported before. On the other hand, the crystal can be grown more easily than CMTC.

3. Disscussion

In this crystal, the cadmium ions are octahedrally surrounded by four NCS ligands and two DMSO ligands through N and O atoms respectively, the mercury ions are tetrahedrally surrounded by four SCN ligands. In crystal CMTC, cadmium and mercury are tetrahedrally surrounded by four SCN ligands through N atoms and S atoms, respectively. Because of the formation of the octahedron, the efficiency of CMTD crystal powder SHG is larger than that of CMTC crystal. These can be explained well by the double-radical structure model theory. In the octahedral environment, there are two O atoms (of dimethyl sulfoxide) in the coordination atoms increasing the distortion degree and the degree of ionization is also enhanced, so the crystal CMTD has a larger X_{ijk} than that of CMTC. Just because of the formation of the octahedron, crystal CMTD has a violet-shift of 18nm compared with CMTC.

Table 2: Final Coordinates and Equivalent Isotropic Displacement Parameters of the non-Hydrogen atoms

Atom	x	y	z	U(eq) [Ang^2]
Hg	-0.00621(6)	0.76141(6)	0.12416(2)	0.0560(2)
Cd	0.48117(12)	0.26428(11)	0.12577(3)	0.0383(3)
S1	0.5897(4)	0.2339(5)	0.01462(13)	0.0613(14)
S2	0.5082(5)	0.1614(4)	0.23759(13)	0.0596(14)
S3	-0.0028(6)	0.9883(5)	0.18238(17)	0.0803(18)
S4	-0.0094(5)	0.5009(4)	0.16720(17)	0.0660(16)
S5	0.2472(5)	0.7785(6)	0.07683(16)	0.0700(16)
S6	-0.2469(5)	0.7876(7)	0.07257(17)	0.0763(16)
O1	0.4453(11)	0.2340(12)	0.0466(3)	0.060(3)
O2	0.5012(12)	0.3037(10)	0.2055(3)	0.061(4)
N1	0.6018(16)	0.0193(15)	0.1240(5)	0.069(5)
N2	0.3860(15)	0.5120(14)	0.1153(5)	0.055(5)
N3	0.7328(15)	0.3686(15)	0.1202(5)	0.063(5)
N4	0.2436(16)	0.1527(16)	0.1399(5)	0.067(5)
C1	0.568(3)	0.413(2)	-0.0204(9)	0.157(15)
C2	0.550(3)	0.087(3)	-0.0281(7)	0.134(11)
C3	0.679(2)	0.179(3)	0.2701(7)	0.119(12)
C4	0.380(2)	0.205(2)	0.2832(6)	0.090(8)
C5	0.6662(17)	-0.0712(18)	0.1040(6)	0.052(6)
C6	0.3298(19)	0.6191(19)	0.0987(5)	0.051(6)
C7	0.1452(18)	0.0862(17)	0.1578(5)	0.051(5)
C8	0.8419(19)	0.4214(17)	0.1405(6)	0.051(5)

U(eq) = 1/3 of the trace of the orthogonalized U Tensor

Table 3: The bond angle (°) and distances (Å) of CMTD

Bond angles (°)			
S3-Hg-S4	111.07(15)	Hg-S4-C8	98.8(6)
S3-Hg-S5	106.64(16)	Hg-S5-C6	96.8(6)
S3-Hg-S6	108.34(17)	Hg-S6-C5	96.8(6)
S4-Hg-S5	108.13(15)	Cd-O1-S1	118.3(5)
S4-Hg-S6	110.21(16)	Cd-O2-S2	118.3(5)
S5-Hg-S6	112.42(15)	Cd-N1-C5	149.2(13)
O1-Cd-O2	176.1(3)	Cd-N2-C6	161.9(13)
O1-Cd-N1	86.3(4)	Cd-N3-C8	147.0(13)
O1-Cd-N2	86.0(4)	Cd-N4-C7	161.6(13)
O1-Cd-N3	95.8(4)	S6-C5-N1	176.5(15)
O1-Cd-N4	90.3(4)	S5-C6-N2	177.5(14)
O2-Cd-N1	96.9(4)	S3 -C7-N4	178.0(14)
O2-Cd-N2	91.0(4)	S4-C8-N3	177.6(14)
O2-Cd-N3	86.6(4)	O2-Cd-N4	87.4(4)
N1-Cd-N2	169.9(5)	N1-Cd-N3	86.3(5)
N1-Cd-N4	91.1(5)	N2-Cd-N3	87.9(4)
N2-Cd-N4	95.4(5)	N3-Cd-N4	173.2(5)
O1-S1-C1	103.7(9)	O1-S1-C2	104.4(9)
C1-S1-C2	101.8(11)	O2-S2-C3	106.3(9)
O2-S2-C4	104.3(7)	C3-S2-C4	96.8(9)
Hg-S3-C7	97.0(5)		
Bond distances (Å)			
Hg-S3	2.541(5)	S1-C2	1.77(2)
Hg-S4	2.535(4)	S2-O2	1.517(9)
Hg-S5	2.543(4)	S2-C3	1.727(18)
Hg-S6	2.525(5)	S2-C4	1.729(17)
Cd-O1	2.270(9)	S3-C7_d	1.664(16)
Cd-O2	2.282(9)	S4-C8_a	1.623(17)
Cd-N1	2.331(13)	S5-C6	1.652(17)
Cd-N2	2.285(12)	S6-C5_b	1.670(17)
Cd-N3	2.327(13)	N1-C5	1.10(2)
Cd-N4	2.272(14)	N2-C6	1.13(2)
S1-O1	1.526(10)	N3-C8	1.18(2)
S1-C1	1.83(2)	N4-C7	1.13(2)

4. Conclusion

In summary, CMTD crystal is a novel NLO complex material, the efficiency of this crystal powder SHG is larger than that of CMTC crystal. It belongs to the orthorhombic system, space group $P2_12_12_1$ and point group 222. The unit cell parameters are: a= 8.5188(6) Å, b=8.5398(7) Å, c=28.224(6) Å, V=2053.3(5) $Å^3$, Z=4 and Dm=2.270 g/cm^3. Colorless, high optical quality single crystals of CMTD can be grown if the small crystal without

macrodefects is used to be seed. The crystal is transparent from 360 nm to 2260 nm and can be grown more easily than CMTC.

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