Crystal structure of cadmium mercury tetrathiocyanate (glycol monomethyl ether), $C_7H_8CdHgN_4O_2S_4$

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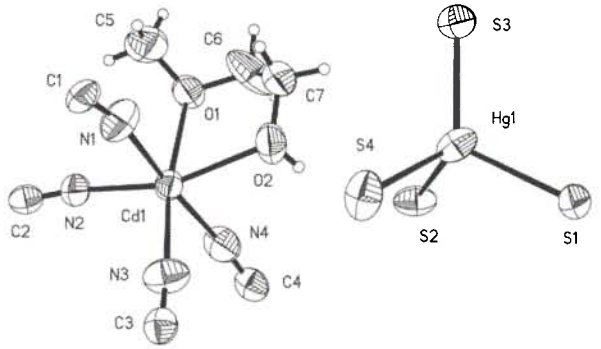
Received December 13, 1999, CCDC-No. 1267/367



Abstract

$C_7H_8CdHgN_4O_2S_4$, orthorhombic, $Pca2_1$ (No. 29), a = 16.432(2) Å, b = 7.3794(9) Å, c = 13.471(1) Å, V = 1633.5 Å^3, Z = 4, $R_{gt}(F)$ = 0.036, $wR_{ref}(F^2)$ = 0.092, T = 293 K.

Source of material

To a crystaline powder of $CdHg(SCN)_4$ was added a mixed solvent of glycol monomethyl ether and water (volume ratio: 1:1). This mixture was heated and stirred until $CdHg(SCN)_4$ was dissolved. The colorless solution was left at room temperature.The deposited crystals were separated.

Discussion

Recently, organometallic complexes have attracted much attention, and there is corresponding studied on these complexes for the exploration of efficient second harmonic generate (SHG) materials because of their high nonlinearity, physico-chemical stability and structure flexibility [1, 2]. Many new organometallic nonlinear optic (NLO) materials were found based on the idea of combining inorganic distorted polyhedron with the asymmetric conjugate system [3-5]. We have previously reported the NLO crystal of cadmium mercury thiocyanate (CMTC) [5], which may generate second harmonic blue-viole light by using GaAlAs laser diodes pump.

Here, we report crystal structure, and properties of the other thiocyanate complex, cadmium mercury tetra(thiocyanate) (glycol monomethyl ether). However, the properties of the new crystal have some better character than these of CMTC. It has higher NLO effect, and is easy to grow as large-size crystals, and still use as a pyroelectric crystal. According to the hard and soft acid and base concept, the soft cations prefer to coordinate with soft base or acid while the hard acid or base is easier to coordinate with the hard cations [6-9]. So in this structure, the Hg^{2+} is coordinated with four SCN sulfur atoms and is in a tetrahedral environment. The Cd^{2+} is hexa-coordinated. It is coordinated with glycol monomethyl ether (GME) molecule and four SCN nitrogen atoms. The average Hg—S lengths are 2.549 Å. The average bond angles around the mercury atoms are 109°(maxium 116.82(13)° and minimam 98.68(14)°). The average Cd—N and Cd—O bond lengths are 2.272 Å and 2.370 Å, respectively. The average bond angles, N–Cd–O and N–Cd–N are 108.8° and 106.5°, respectively. The angles O–Cd–O are 71.8(4)°. The participation of the GME adduct base leadsto much more distortion than the original crystal CMTC. GME combines in the form of bidentate ligand with Cd to form a five-membered chelate ring. The five-membered chelate ring and distorted polyhedron may be a reason for good nonlinear optical property [10]. The most stricking features are the -S=C=N- bridges which connect Cd and Hg, forming an inifinite three-dimensional network. The distorted tetrahedra HgS_4 and octahedra CdN_4O_2, donate larger polarization, which in turn, we believe, induces greater non-linearity.

Table 1. Data collection and handling.

Crystal:	colourless prism, size 0.20 × 0.22 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	112.00 cm^{-1}
Diffractometer, scan mode:	Bruker P4, ω/2θ
$2\theta_{max}$:	52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2037, 1670
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1506
$N(param)_{refined}$:	173
Program:	SHELXTL [11]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(2A)	4a	0.6281	–0.1383	0.6741	0.073
H(5A)	4a	0.3342	–0.1996	0.7296	0.126
H(5B)	4a	0.3556	–0.0385	0.6583	0.126
H(5C)	4a	0.3373	–0.0010	0.7707	0.126
H(6A)	4a	0.5107	–0.3243	0.7563	0.114
H(6B)	4a	0.4363	–0.3471	0.6848	0.114
H(7A)	4a	0.4966	–0.1906	0.5679	0.097
H(7B)	4a	0.5572	–0.3406	0.6045	0.097

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Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	4*a*	0.75480(3)	–0.36200(7)	0.50051(6)	0.0371(3)	0.0619(4)	0.0580(4)	–0.0066(2)	–0.0038(3)	0.0152(4)
Cd(1)	4*a*	0.53555(5)	0.1405(1)	0.7455(1)	0.0378(4)	0.0383(4)	0.0478(5)	0.0018(3)	–0.0008(5)	0.0019(6)
S(1)	4*a*	0.8975(2)	–0.4583(6)	0.4598(3)	0.045(2)	0.066(2)	0.059(2)	0.009(2)	–0.006(2)	–0.022(2)
S(2)	4*a*	0.7490(2)	–0.3749(5)	0.6981(3)	0.059(2)	0.071(3)	0.042(2)	–0.022(2)	–0.006(2)	0.007(2)
S(3)	4*a*	0.6432(2)	–0.5607(5)	0.4403(3)	0.053(2)	0.042(2)	0.057(2)	–0.004(1)	–0.009(2)	0.008(2)
S(4)	4*a*	0.7415(2)	–0.0222(6)	0.4782(3)	0.062(2)	0.056(2)	0.075(3)	0.010(2)	0.017(2)	0.020(2)
O(1)	4*a*	0.4427(6)	–0.106(1)	0.746(2)	0.045(5)	0.053(5)	0.084(9)	–0.010(4)	0.017(8)	–0.020(8)
O(2)	4*a*	0.5895(6)	–0.092(1)	0.6450(9)	0.058(5)	0.050(5)	0.074(7)	0.009(4)	0.014(5)	–0.006(5)
N(1)	4*a*	0.4699(7)	0.245(2)	0.606(1)	0.054(7)	0.079(9)	0.059(8)	0.012(7)	–0.004(6)	0.014(8)
N(2)	4*a*	0.4470(6)	0.296(2)	0.839(1)	0.044(5)	0.062(7)	0.07(1)	0.011(5)	–0.002(6)	–0.024(7)
N(3)	4*a*	0.6364(8)	0.344(2)	0.720(1)	0.061(7)	0.068(7)	0.058(8)	–0.022(6)	–0.004(6)	0.020(7)
N(4)	4*a*	0.6132(9)	0.029(2)	0.871(1)	0.093(9)	0.050(7)	0.063(8)	0.008(7)	–0.031(8)	0.005(7)
C(1)	4*a*	0.4398(6)	0.329(2)	0.546(1)	0.027(5)	0.053(7)	0.054(7)	0.000(5)	0.001(5)	0.002(7)
C(2)	4*a*	0.4084(7)	0.402(2)	0.882(1)	0.041(6)	0.051(7)	0.044(7)	–0.011(5)	0.003(6)	0.006(7)
C(3)	4*a*	0.6841(8)	0.455(2)	0.710(1)	0.050(6)	0.049(7)	0.040(6)	0.005(6)	–0.003(6)	0.004(6)
C(4)	4*a*	0.6738(9)	0.006(2)	0.914(1)	0.071(8)	0.037(6)	0.049(8)	–0.002(6)	–0.006(7)	0.012(6)
C(5)	4*a*	0.361(1)	–0.085(2)	0.725(2)	0.07(1)	0.066(9)	0.11(2)	–0.022(8)	–0.01(1)	0.00(1)
C(6)	4*a*	0.479(1)	–0.264(2)	0.705(2)	0.14(2)	0.055(9)	0.09(1)	–0.05(1)	0.05(1)	–0.02(1)
C(7)	4*a*	0.5296(9)	–0.230(3)	0.624(2)	0.059(9)	0.08(1)	0.11(2)	0.005(8)	–0.002(9)	–0.04(1)

Acknowledgments. This work is supported by grants from the "863" and the National Natural Science Foundation of China.

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