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R. Chitra, Pascal Roussel, R.R. Choudhury. Thiourea:diethyl oxalate(2:1) complex: Single crystal diffraction at 100K. 52nd DAE (Departement of Atomic Energy) Solid State Physics Symposium (SSPS-2007), 2007, Mysore, India. <hal-00187593>

HAL Id: hal-00187593

https://hal.archives-ouvertes.fr/hal-00187593

Submitted on 14 Nov 2007

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Thiourea:diethyl oxalate(2:1) complex: Single crystal diffraction at 100k

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Abstract

The crystal structure of thiourea:diethyl oxalate at 100k was solved using single crystal x-ray diffraction. The system crystallized in triclinic system, similar to that at room temeperature. No phase transition is observed at low temperature. The R-factor obtained was $R[F^2 > 2\sigma(F^2)] = 0.03$. *The crystal structure at low temperature induces closer packing of the molecules and general shrinkage of the unit cell and shortening of the hydrogen bonds to the by about 2%*.

INTRODUCTION

A host-guest system typically consists of a host molecule with the guest binding to it with non-covalent interactions. These systems are interesting from the viewpoint of intermolecular interactions. The intermolecular interactions play a definitive role in crystal engineering [1]. Their varied strength helps in designing new crystals. Thiourea molecule forms range of host-guest systems, due to its planar nature with guests of appropriate size and shape [2,3]. One such system studied by us is the thiourea:oxalate ester systems. These systems were found to undergo phase transitions above room temperature, which have been studied using Raman spectroscopy [4, 5]. The room temperature structures of thiourea: diethyl and thiourea:dimethyl oxalate were reported by us[6, 7]. The structure at 100K of thiourea:dimethyl oxalate also was reported [6]. As the two complexes are isostructural, low temperature study of thiourea: diethyl oxalate was taken up for comparison.

CRYSTALLIZATION

Colorless single crystals of the thiourea:diethyl oxalate(2:1) were grown from ethanol solution containing thiourea and oxalic acid in stoichiometric amounts. Crystal of approximately 0.3mm was used for data collection.

EXPERIMENT

The details of data collection are summarized in table 1 using Mo K_α radiation.

Table 1. Data Collection details

Bruker Smart CCD area detector diffractometer	$\theta_{max} = 27.8°$
ϕ and ω	$h = -8 \rightarrow 8$
Absorption correction: none	$k = -9 \rightarrow 9$
$T_{min} = 0.0$, $T_{max} = 0.0$	$l = -10 \rightarrow 10$
2574 measured reflections	$R_{int} = 0.015$
1401 independent reflections	1329 reflections with $I > 2\sigma(I)$

STRUCTURE DETERMINATION

The approximate structure was determined using SHELXS direct methods. The atomic parameters so obtained were subjected to a series of isotropic and anisotropic full matrix least square refinements using SHELXL. All the reflections were used for refinement. In the initial stages of refinement weight (w) was taken to be $1/\sigma(F_o^2)$ which was derived using counting statistics. From the difference Fourier map all the hydrogen atoms were located and refined isotropically. The asymmetric unit consisted of one complete thiourea molecule and one half of a diethyl oxalate molecule lying on an inversion center All the non-hydrogen thermal parameters were refined anistropically. The refinement details and crystal data are summarized in tables 2a & 2b respectively. Fig. 1. shows the Ortep picture of the refined structure.

Table 2a Refinement Details

Refinement on F^2	$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.081$	$S = 1.09$
1401 reflections	118 parameters
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0487P)^2 + 0.1387P]$ where $P = (F_o^2 + 2F_c^2)/3$	

Table 2b Crystal Data

$C_4H_9N_2O_2S$	V = 338.1 Å^3
M_r = 149.19	Z = 2
D_x = 1.465 Mg m^{-3}	Mo $K\alpha$ radiation
a = 7.065 Å, b = 7.406 Å, c = 8.259 Å, α = 63.61°,β = 67.70°,γ = 63.76°	μ = 0.41 mm^{-1}
Temperature:100k	Irregular shape and colourless

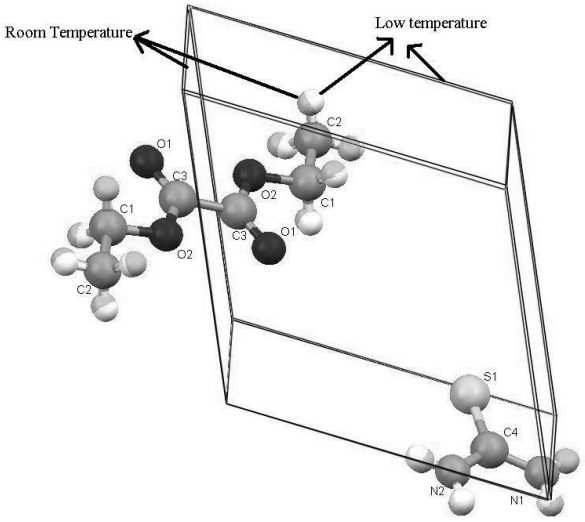

Figure. 1. Ortep picture with 50% ellipsoidal probablity

RESULTS AND DISCUSSION

A comparison of the cell parameter of this complex at room temperature and at 100k shows that there is shrinkage of the unit cell parameters and unit cell volume to the extent of 1-2% as observed in thiourea:diethyl oxalate complex. The packing of the molecule in the unit cell at room temperature and at 100k is shown in Figure 1. Equation of the plane was constructed both for the thiourea including the hydrogen atoms and for the ester moiety. It is observed that all the atoms of the thiourea moiety are planar, with maximum deviation occurring for the hydrogen atoms in particular, atom H3 deviates the maximum. Among the atoms of the ester plane, C1 deviates the maximum from the least squares plane. The angle between the two planes was 2.40°(6), with both the molecules lying almost in the same plane. The hydrogen bonding parameters of the complex are given in Table 3.

Table 3 Hydrogen bond parameters (°, Å)

	D—H	H...*A*	D...A	*D*—H...*A*
N1—H1...S1^{i}	0.93 (2)	2.57 (2)	3.4996 (14)	172.8 (16)
N1—H2...O1^{ii}	0.87 (2)	2.46 (2)	3.2036 (17)	143.9 (17)
N1—H2...O2^{iii}	0.87 (2)	2.48 (2)	3.2642 (15)	150.9 (18)
N2—H3...O1^{ii}	0.88 (3)	2.08 (3)	2.9245 (17)	159 (2)
N2—H4...S1^{ii}	0.85 (2)	2.62 (2)	3.4683 (14)	174.7 (19)
C2—H8...S1^{iv}	0.94 (2)	2.923 (2)	3.3488 (16)	108.8 (13)

A comparison of the hydrogen bond parameters at room temperature and at 100K shows that the hydrogen bonds involved with the S atom as acceptor are shortened the most. The terminal CH_3 group is involved in C-H..S interaction (Table 3). A comparison of the hydrogen bonds between the isostructural complex of thiourea: dimethyl oxalate shows that the interaction between the neighboring thiourea molecules through N-H..S bonds are longer in the present complex.

CONCLUSION

The title complex is host guest system with thiourea acting as a host and the ester moiety acting as a guest. The crystal structure at low temperature induces closer packing of the molecules and general shrinkage of the unit cell and shortening of the hydrogen bonds to the by about 2%. There is no phase transition at low temperatures. The N-H...S hydrogen bonds between the neighboring thiourea molecules in the present complex are longer compared to the isostructural thiourea: dimethyl oxalate complex.

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