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Synthesis and Crystal Structure of Diethyl Dithiocarbamate Tellurium

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Diethyl dithiocarbamate tellurium was synthesized and characterized by IR spectra, elemental analysis. and single-crystal X-ray diffraction analysis. The crystal structure of tellurium complex was determined by single-crystal X-ray. The possessing parameters: P2(1)/c, a = 15.1640(3) Å, b = 8.4055(2)Å, c = 14.7887(2)Å, α = 90º, β = 117.228(10)º, γ = 90º, V = 1676.1(6)$Å^3$, Z = 4, Mr = 424.12, Dc = 1.681 g/cm^3, μ = 2.256 mm^{-1}, F(000) = 840, T = 296(2)K, R_1 = 0.0246, wR_2 = 0.0603 for 3799 reflections with I > 2σ(I).

Key Words: Diethyl dithiocarbamate tellurium, Crystal structure.

INTRODUCTION

Dithiocarbamates have found wide practical application as antioxidants and lubricants, as vulcanizing and NO-trapping agents[1], as agents for the froth flotation process of sulfide minerals and for the liquid-liquid extraction of transition metals[2,3]. It has also been found that the extraction efficiency of dithiocarbamate complexes rises in the presence of neutral N, S, O, P-donor molecules, which could potentially imply formation of adducts[4]. Besides that, nitrogen donor adducts of dithiocarbamate complexes are also widely used in the preparation of thin semiconductor[5-7] and electroluminescent[8,9] films of transition metal sulfides, the basis of electronics and solar cell technology[10]. The dithiocarbamate anion ($R^1R^2NCS^{2-} = I^-$) is known to be a strong nucleophile and to form stable complexs with many post-transition metals[11]. Thus, complexes involving the Te(IV), Te(II) and Se(II) centres have been reported and structural studies on these have shown the presence of bidentate chelating ligand[12]. In present paper, the synthesis and crystal structure of diethyl dithiocarbamate tellurium are reported.

EXPERIMENTAL

Tellurium dioxide, diethylamine, carbon disulfide, hydrochloric acid and sodium hydroxide was prepared in our laboratory. All the reagents and solvents were commercially available and mostly of analytic grade materials used as supplied, without further purification. IR spectrum was recorded on an Neuxs-830 spectromer. Elemental analyses were performed on a Perkin-Elmer 240 elemental analyzer.

Synthesis: 200 mL water, sodium hydroxide (4 g, 0.1 mol) and diethylamine (7.3 g, 0.1 mol) were added to three neck flask in icewater bath with stirring. Then added carbon disulfide (7.8 g, 0.1 mol) after 20 min and continued to react for *ca.* 4 h to obtain a light yellow liquid. The light yellow liquid is diethyl dithiocarbamate sodium. Tellurium dioxide (4 g, 0.025 mol) was dissolved with sodium hydroxide (2 g, 0.05 mol) and added 3 mL hydrochloric acid to it. Then droped into diethyl dithiocarbamate sodium with stirring and controlled on the condition of alkalescence in the reaction. A yellow deposition of diethyl dithiocarbamate tellurium was obtained. They were collected by vacuum filtration, washed with a large amount of water and dried in vacuum.

Then recrystallize diethyl dithiocarbamate tellurium with cyclohexane. 6 mL chloroform and 30 mL methanol were mixed in the laboratory. Diethyl dithiocarbamate tellurium (10 mmol) was added into the mixture. A yellow solution was obtained after dissolution and filtration. After standing at room temperature for 2 weeks, well-shaped yellow single crystals were obtained by slow evaporation. IR spectrum (KBr, cm^{-1}): 2978, 2926, 2861 $\nu(CH_3)$, $\nu(CH_2)$, 570 $\nu(C=S)$, 1353 $\nu(C-N)$, 1642 $\nu(C=S)$. Elemental analysis: confirmed the organic content (Found: (%) C, 28.04; H, 4.630; N, 6.482; S, 30.25. Calcd. (%) for $(C_5H_{10}S_2N)_2Te$: C, 28.29; H, 4.716; N, 6.602; S, 30.18).

Crystal structure determination: A yellow crystal having approximate dimensions of 0.30 mm × 0.22 mm × 0.13 mm was selected and mounted on a glass fiber in a random orientation for X-ray diffraction study. Diffraction experiments were performed on a Siemens SMART CCD area-detector diffractometer with graphite-monochromatic MoKα radiation (λ = 0.71073 Å) at temperature 296(2) K, scan technique $1.51° \leq \theta \leq 27.50°$. A total of 16020 reflections were collected, of which 3799 reflections were unique with $R_{int} = 0.0225$. Lp effects and empirical absorption were applied in data corrections. The structure was solved by direct methods and expanded using Fourier techniques and SHELXS-97 program system was used in the solution and refinement of the structure. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added according to theoretical model. The final full-matrix least-squares refinement including 153 variable parameters for 3799 reflections with $I > 2\sigma(I)$ and converged with unweighted and weighted agreement factors of $R_1 = \Sigma(||F_0|-|F_c||)/S|F_0| = 0.0246$ and $wR_2 = \{\Sigma[w(F_0^2-F_C^2)^2]/\Sigma w(F_0^2)^2\}^{1/2} = 0.0603$, where $w = 1/[\sigma^2(F_0^2) + (0.0310P)^2 + 0.6788P]$ and $P = (F_0^2 + 2F_C^2)/3$. The maximum and minimum peaks on the final difference Fourier map are corresponding to 0.798 and -0.645 e/Å^3, respectively.

RESULTS AND DISCUSSION

The atomic coordinates and thermal parameters are listed in Table-1 and the selected bond lengths and bond angles are presented in Table-2. Fig. 1 shows the molecular structure of the title compound. Fig. 2 shows the packing diagram of the title compound, diethyl dithiocarbamate tellurium. From the Fig. 1, it is clear that

TABLE-1
ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^3$ Å^2)

Atom	X	Y	Z	U (eq)
Te	1965(1)	687(1)	581(1)	47(1)
S(1)	3716(1)	1601(1)	1126(1)	52(1)
S(2)	3181(1)	829(1)	2763(1)	62(1)
S(3)	1952(1)	875(1)	-1122(1)	51(1)
S(4)	101(1)	-37(1)	-1073(1)	61(1)
N(1)	5015(2)	1527(3)	3068(2)	56(1)
N(2)	272(2)	280(3)	-2782(2)	55(1)
C(1)	4064(2)	1334(3)	2417(2)	49(1)
C(2)	5754(2)	2024(4)	2740(2)	67(1)
C(3)	6201(3)	630(4)	2440(3)	85(1)
C(4)	5407(3)	1144(4)	4159(2)	72(1)
C(5)	5515(3)	2569(5)	4808(3)	92(1)
C(6)	704(2)	355(3)	-1771(2)	49(1)
C(7)	797(2)	660(4)	-3378(2)	64(1)
C(8)	1133(3)	-804(4)	-3718(3)	83(1)
C(9)	-766(2)	-242(4)	-3366(2)	65(1)
C(10)	-1490(2)	1109(5)	-3699(3)	81(1)

TABLE-2
SELECTED BOND DISTANCES (Å) AND ANGLES (º) DISTANCES

Bond	Bond length	Bond	Bond length
Te(1)-S(3)	2.514(6)	S(2)-C(1)	1.691(3)
Te(1)-S(1)	2.515(7)	S(3)-C(6)	1.742(3)
Te(1)-S(4)	2.832(7)	S(4)-C(6)	1.695(3)
Te(1)-S(2)	2.896(7)	N(1)-C(1)	1.327(3)
S(1)-C(1)	1.747(2)	N(2)-C(6)	1.330(3)
Bond	**Angles**	**Bond**	**Angles**
S(3)-Te(1)-S(1)	79.98(2)	C(1)-N(1)-C(4)	121.8(2)
S(3)-Te(1)-S(4)	66.49(2)	C(2)-N(1)-C(4)	115.8(2)
S(1)-Te(1)-S(4)	146.40(2)	C(6)-N(2)-C(7)	122.8(2)
S(3)-Te(1)-S(2)	145.40(2)	C(6)-N(2)-C(9)	121.2(2)
S(1)-Te(1)-S(2)	65.76(2)	C(7)-N(2)-C(9)	116.1(2)
S(4)-Te(1)-S(2)	147.82(2)	N(1)-C(1)-S(2)	123.97(18)
C(1)-S(1)-Te(1)	93.37(9)	N(1)-C(1)-S(1)	117.53(18)
C(1)-S(2)-Te(1)	82.06(8)	S(2)-C(1)-S(1)	118.49(15)
C(6)-S(3)-Te(1)	92.57(9)	N(2)-C(6)-S(4)	123.3(2)
C(6)-S(4)-Te(1)	83.14(9)	N(2)-C(6)-S(3)	118.9(2)
C(1)-N(1)-C(2)	122.3(2)	S(4)-C(6)-S(3)	117.79(15)

all bond lengths and angles are within normal ranges. It contains two tetra-atomic rings, the two rings [Te(1)-S(1)-N(1)-S(2) and Te(1)-S(3)-N(6)-S(4)] are nearly coplanar structure, with S(3)-Te(1)-S(1) 79.98(2), S(1)-Te(1)-S(2) 65.76(2), S(4)-Te(1)-S(2) 147.82(2), S(3)-Te(1)-S(4) 66.49(2). The plane of S(1)-S(2)-S(3)-S(4) is approximately a trapezia, with Te(1)-S(3) 2.514(6), Te(1)-S(1) 2.515(7), Te(1)-

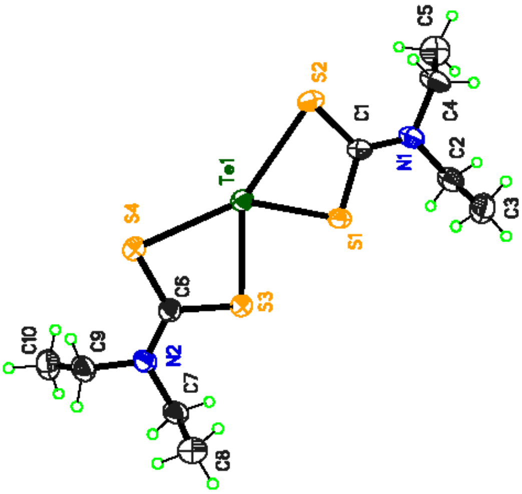

Fig. 1. Molecular structure of diethyl dithiocarbamate tellurium

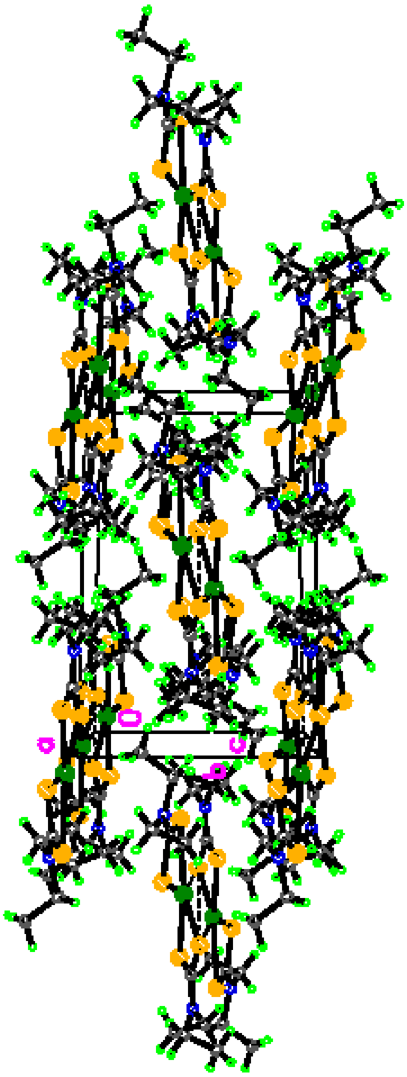

Fig. 2. Molecular packing arrangement in the unit cell

S(4) 2.832(7), Te(1)-S(2) 2.896(7). The crystal packing is stabilized by bonds interaction. The centroid (Te1) of a molecular has the weak Te...S...S interactions with another molecular, respectively.

Conclusion

Crystal structure of diethyl dithiocarbamate tellurium has been synthesized and characterized by IR, elemental analysis and X-ray diffraction analysis. Crystal structure determination plays an important role on curing promotion mechanism.

Supplementary material: Crystallographic data for the structure reported in this communication have been deposited with Cambridge Crystallographic Data Center as supplementary publication No. CCDC-708932.

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