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The crystal and molecular structure of dimethyldithiocarbamato-2-(2-quinolinyl)phenyltellurium(II)

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Abstract

The crystal structure of dimethyldithiocarbamato-2(2-quinolinyl)phenyltellurium (II) has been determined from three dimensional X-ray counter data. The crystal system is triclinic, space group $P\bar{1}$ with a 7.360(5), b 15.022(10), c 17.730(10) Å, α 114.26(2)°, β 94.12(6)°, γ 95.63(3)°, $Z = 4$, R 3.36% for 4969 observed reflections; For two independent molecules, the coordination about Te can be considered to be trigonal bipyramidal, with a carbon atom and the two lone pairs of Te comprising the equatorial coordination, and sulphur together with the quinolinyl nitrogen atom in axial positions. (Te $\cdots$ C 2.124(5), 2.135(4); Te $\cdots$ N 2.365(4), 2.385(4); Te $\cdots$ S(1) 2.569(1), 2.543(1) Å). S(2) makes a weak secondary interaction with Te (3.222(1), 3.230(1) Å) in the C,N,S(1) plane. There are no significant intermolecular contacts.

Introduction

The preparation and chemical properties of the title compound have previously been reported by Al-Salim et al. [1]. Following earlier structural studies of analogous complexes in which short Te–N interactions were found [1,2], we now examine the effect of the tellurium oxidation state and of the type of ligand *trans* to nitrogen on the Te–N interaction.

X-ray structure analysis

After a preliminary study by photographic methods, cell parameters and reflection intensities were measured with graphite monochromated Mo-K_α radiation from a yellow/orange crystal, 0.60 × 0.30 × 0.25 mm, using an Enraf–Nonius CAD-4 diffractometer, operating in the ω–2θ scan mode. Three standard reflections were monitored at regular intervals to check the stability of the system. 6400 reflections were scanned in the range $2 < \theta < 25°$. Lorentz and polarization factors were applied to the data, and 4969 unique reflections with $I > 2.5\sigma(I)$ were used in the structural analysis. The crystals were triclinic with no systematic absences, the centrosymmetric space group $P\bar{1}$ being established by the successful analysis.

Crystal data

$C_{18}H_{16}N_2S_2Te$, $M_r = 452.1$, space group $P\bar{1}$, a 7.360(5), b 15.022(10), c 17.730(10) Å, α 114.26(2)°, β 94.12(6)°, γ 95.63(3)°, V 1764.9 Å^3, $Z = 4$, D_c 1.701 g cm^{-3}, $F(000) = 888$, λ(Mo-K_α) 0.71069, μ 1.97 mm^{-1}.

The atomic coordinates for tellurium and for most of the lighter atoms were found by direct methods using SHELX86 [3]. The remaining non-hydrogen atoms were located by a Fourier difference synthesis. As only some of the hydrogens could be located from difference maps, all the hydrogen atoms were placed in calculated positions (C–H 1.08 Å) and allowed to "ride" on their respective carbon atoms in the subsequent least-squares refinements. The weighting scheme used was $w = 1/[\sigma^2(F) + 0.0006F^2]$ and the refinements converged to $R = 0.0336$ and $R_w = 0.0485$, when all shifts were $< 0.1\sigma$.

Non-hydrogen atomic coordinates are listed in Table 1 and bond lengths and angles in Table 2. Computations were carried out on the Birmingham University

Table 1

Fractional atomic coordinates (×10^5 for tellurium and ×10^4 for all other non-hydrogen atoms) with e.s.d.'s in parentheses

	x	y	z		x	y	z
Te(1A)	29856(3)	73451(2)	222(2)	Te(1B)	28125(3)	72503(2)	50311(2)
S(1A)	3022(2)	9211(1)	507(1)	S(1B)	1843(2)	8876(1)	5985(1)
S(2A)	2202(2)	8190(1)	−1354(1)	S(2B)	−882(2)	7902(1)	4443(1)
N(1A)	2858(4)	5744(2)	−24(2)	N(1B)	4565(5)	5930(3)	4422(2)
N(2A)	2200(5)	10102(2)	−448(2)	N(2B)	−1156(5)	9572(2)	5738(2)
C(1A)	3740(5)	7560(3)	1271(3)	C(1B)	5187(6)	7549(3)	5913(3)
C(2A)	4352(6)	8476(3)	1926(3)	C(2B)	5444(7)	8327(4)	6694(3)
C(3A)	4865(7)	8556(4)	2721(3)	C(3B)	7043(8)	8525(4)	7220(4)
C(4A)	4735(7)	7730(5)	2884(3)	C(4B)	8395(9)	7945(5)	6965(4)
C(5A)	4125(7)	6813(4)	2245(3)	C(5B)	8182(7)	7156(4)	6200(4)
C(6A)	3641(5)	6713(3)	1428(3)	C(6B)	6532(6)	6940(4)	5663(3)
C(7A)	3074(5)	5747(3)	729(3)	C(7B)	6204(6)	6086(3)	4845(3)
C(8A)	2732(7)	4844(4)	813(3)	C(8B)	7529(8)	5427(4)	4501(4)
C(9A)	2150(6)	4003(4)	145(3)	C(9B)	7076(9)	4660(5)	3775(5)
C(10A)	1897(5)	3977(3)	−667(3)	C(10B)	5288(8)	4466(4)	3294(4)
C(11A)	2302(5)	4891(3)	−722(3)	C(11B)	4050(7)	5142(3)	3662(3)
C(12A)	2151(7)	4898(3)	−1517(3)	C(12B)	2274(7)	4985(3)	3233(3)
C(13A)	1547(8)	4042(3)	−2222(3)	C(13B)	1722(9)	4191(3)	2487(3)
C(14A)	1078(7)	3164(4)	−2162(4)	C(14B)	2986(11)	3525(4)	2135(4)
C(15A)	1273(7)	3123(3)	−1407(4)	C(15B)	4709(10)	3665(4)	2523(4)
C(16A)	2452(5)	9221(3)	−465(3)	C(16B)	−199(6)	8824(3)	5387(3)
C(17A)	1825(7)	10215(4)	−1225(3)	C(17B)	−2876(7)	9632(4)	5307(4)
C(18A)	2392(6)	11002(3)	319(3)	C(18B)	−576(7)	10369(3)	6577(3)

Table 2

Bond lengths (Å) and bond angles (°) with e.s.d.'s in parentheses

Te(1A)–S(1A)	2.569(1)	Te(1B)–S(1B)	2.543(1)
Te(1A)...S(2A)	3.222(1)	Te(1B)...S(2B)	3.230(1)
Te(1A)–N(1A)	2.365(4)	Te(1B)–N(1B)	2.385(4)
Te(1A)–C(1A)	2.124(5)	Te(1B)–C(1B)	2.135(4)
S(1A)–C(16A)	1.751(5)	S(1B)–C(16B)	1.752(5)
S(2A)–C(16A)	1.677(40	S(2B)–C(16B)	1.676(4)
N(1A)–C(7A)	1.331(7)	N(1B)–C(7B)	1.320(6)
N(1A)–C(11A)	1.365(4)	N(1B)–C(11B)	1.373(5)
N(2A)–C(16A)	1.343(6)	N(2B)–C(16B)	1.338(5)
N(2A)–C(17A)	1.465(8)	N(2B)–C(17B)	1.461(7)
N(2A)–C(18A)	1.456(5)	N(2B)–C(18B)	1.473(5)
C(1A)–C(2A)	1.390(5)	C(1B)–C(2B)	1.381(6)
C(1A)–C(6A)	1.407(8)	C(1B)–C(6B)	1.386(6)
C(2A)–C(3A)	1.385(8)	C(2B)–C(3B)	1.375(8)
C(3A)–C(4A)	1.381(10)	C(3B)–C(4B)	1.366(9)
C(4A)–C(5A)	1.381(7)	C(4B)–C(5B)	1.371(7)
C(5A)–C(6A)	1.409(8)	C(5B)–C(6B)	1.411(7)
C(6A)–C(7A)	1.465(5)	C(6B)–C(7B)	1.472(6)
C(7A)–C(8A)	1.424(8)	C(7B)–C(8B)	1.443(8)
C(8A)–C(9A)	1.331(6)	C(8B)–C(9B)	1.320(8)
C(9A)–C(10A)	1.421(9)	C(9B)–C(10B)	1.449(9)
C(10A)–C(11A)	1.420(7)	C(10B)–C(11B)	1.418(7)
C(10A)–C(15A)	1.412(6)	C(10B)–C(15B)	1.402(7)
C(11A)–C(12A)	1.410(8)	C(11B)–C(12B)	1.411(7)
C(12A)–C(13A)	1.379(6)	C(12B)–C(13B)	1.367(6)
C(13A)–C(14A)	1.378(8)	C(13B)–C(14B)	1.417(9)
C(14A)–C(15A)	1.363(10)	C(14B)–C(15B)	1.352(10)
S(1A)–Te(1A)–N(1A)	163.7(1)	S(1B)–Te(1B)–N(1B)	162.8(1)
S(1A)–Te(1A)–C(1A)	90.3(1)	S(1B)–Te(1B)–C(1B)	89.0(1)
N(1A)–Te(1A)–C(1A)	74.5(1)	N(1B)–Te(1B)–C(1B)	74.0(1)
Te(1A)–S(1A)–C(16A)	98.6(1)	Te(1B)–S(1B)–C(16B)	99.1(1)
Te(1A)–N(1A)–C(7A)	113.1(2)	Te(1B)–N(1B)–C(7B)	112.7(3)
Te(1A)–N(1A)–C(11A)	124.7(3)	Te(1B)–N(1B)–C(11B)	124.7(3)
C(7A)–N(1A)–C(11A)	121.3(4)	C(7B)–N(1B)–C(11B)	122.1(4)
C(16A)–N(2A)–C(17A)	120.6(3)	C(16B)–N(2B)–C(17B)	121.2(3)
C(16A)–N(2A)–C(18A)	123.2(4)	C(16B)–N(2B)–C(18B)	122.8(4)
C(17A)–N(2A)–C(18A)	116.0(4)	C(17B)–N(2B)–C(18B)	116.0(4)
Te(1A)–C(1A)–C(2A)	124.1(4)	Te(1B)–C(1B)–C(2B)	123.1(4)
Te(1A)–C(1A)–C(6A)	117.0(3)	Te(1B)–C(1B)–C(6B)	117.1(3)
C(2A)–C(1A)–C(6A)	118.9(5)	C(2B)–C(1B)–C(6B)	119.8(4)
C(1A)–C(2A)–C(3A)	120.8(5)	C(1B)–C(2B)–C(3B)	120.9(5)
C(2A)–C(3A)–C(4A)	120.6(4)	C(2B)–C(3B)–C(4B)	119.4(5)
C(3A)–C(4A)–C(5A)	119.7(6)	C(3B)–C(4B)–C(5B)	121.5(5)
C(4A)–C(5A)–C(6A)	120.5(6)	C(4B)–C(5B)–C(6B)	119.3(5)
C(1A)–C(6A)–C(5A)	119.4(4)	C(1B)–C(6B)–C(5B)	119.0(4)
C(1A)–C(6A)–C(7A)	118.7(5)	C(1B)–C(6B)–C(7B)	119.3(4)
C(5A)–C(6A)–C(7A)	121.9(5)	C(5B)–C(6B)–C(7B)	121.7(4)
N(1A)–C(7A)–C(6A)	115.9(5)	N(1B)–C(7B)–C(6B)	115.9(4)
N(1A)–C(7A)–C(8A)	119.7(4)	N(1B)–C(7B)–C(8B)	119.8(4)
C(6A)–C(7A)–C(8A)	124.4(5)	C(6B)–C(7B)–C(8B)	124.3(4)
C(7A)–C(8A)–C(9A)	120.2(6)	C(7B)–C(8B)–C(9B)	119.6(5)
C(8A)–C(9A)–C(10A)	121.3(6)	C(8B)–C(9B)–C(10B)	122.0(6)
C(9A)–C(10A)–C(11A)	116.3(4)	C(9B)–C(10B)–C(11B)	115.8(4)
C(9A)–C(10A)–C(15A)	125.1(5)	C(9B)–C(10B)–C(15B)	125.1(6)
C(11A)–C(10A)–C(15A)	118.5(5)	C(11B)–C(10B)–C(15B)	119.1(5)

(continued)

Table 2 (continued)

N(1A)–C(11A)–C(10A)	121.0(5)	N(1B)–C(11B)–C(10B)	120.7(4)
N(1A)–C(11A)–C(12A)	120.4(4)	N(1B)–C(11B)–C(12B)	120.8(4)
C(10A)–C(11A)–C(12A)	118.6(4)	C(10B)–C(11B)–C(12B)	118.5(4)
C(11A)–C(12A)–C(13A)	120.6(5)	C(11B)–C(12B)–C(13B)	121.6(5)
C(12A)–C(13A)–C(14A)	120.6(6)	C(12B)–C(13B)–C(14B)	118.7(6)
C(13A)–C(14A)–C(15A)	120.4(4)	C(13B)–C(14B)–C(15B)	121.2(5)
C(10A)–C(15A)–C(14A)	121.3(5)	C(10B)–C(15B)–C(14B)	120.8(6)
S(1A)–C(16A)–S(2A)	121.8(3)	S(1B)–C(16B)–S(2B)	121.9(3)
S(1A)–C(16A)–N(2A)	115.6(3)	S(1B)–C(16B)–N(2B)	115.2(3)
S(2A)–C(16A)–N(2A)	122.6(4)	S(2B)–C(16B)–N(2B)	122.9(3)

Honeywell computer and at the University of Manchester Regional Computer Centre with SHELX76 [4] and SHELX86 [3]; Stereoscopic views were drawn using PLUTO [5].

Discussion

The molecular structure is shown in Fig. 1. The structure contains two crystallographically independent molecules within the asymmetric unit. The coordination about tellurium can be considered as essentially ψ-trigonal bipyramidal, with C(1) and the two lone pairs of Te making up the equatorial coordination, and with S(1) and N(1) axial. The distortion of coordination geometry from ideal ψ-trigonal bipyramidal, particularly N(1)–Te–C(1) (74.5(1)° molecule A, 74.0(1)° molecule B) is due to the constraint imposed by the five-membered chelate ring. S(2) makes a weak secondary interaction in the C(1),N(1),S(1) plane, which bisects the angle between the lone pairs. Thus the position *trans* to the bonded phenyl carbon is unoccupied, and the compound can be regarded as almost "T-shaped" [6].

The 2-(2-quinolinyl)phenyl ligand is planar to within ±0.15 Å in molecule A and ±0.10 Å in molecule B, with a twist of 8.3(3)°, 5.3(2)° between the mean planes of

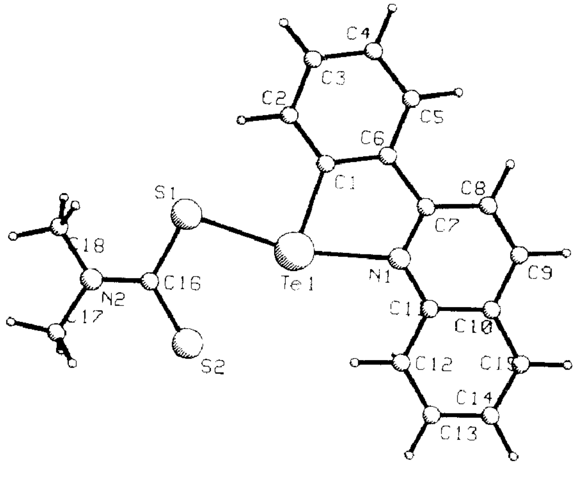

Fig. 1. View of complex A showing the atom numbering. The other molecule in the asymmetric unit (complex B) has virtually identical conformation.

the quinolinyl and phenyl rings. The tellurium atom is displaced 0.33 Å (for A) and 0.38 Å (for B) from this plane; S(1) is displaced by 0.94 Å and 0.78 Å and S(2) by 0.80 Å and 1.07 Å for molecules A and B, respectively. The dimethyldithiocarbamate group is planar and is oriented at angles of 12.0(4)°, 3.9(2)° to the chelate ring plane in the two molecules.

The distance Te–C(1) (2.124(5), 2.135(4) Å) is in good agreement with the sum of the Pauling single bond covalent radii (2.11 Å) [7] and with values reported for analogous Te^{II} complexes, $Te(C_5H_4NPh)(dmdtc)$ [1], $TePh(tu)_2Cl$ [8] and $Te(C_6H_4N_2Ph)(dmdtc)$ [9] (where dmdtc = dimethyldithiocarbamate and tu = thiourea), which lie in the range 2.101–2.111 Å. The Te–N distance (2.365(4), 2.385(4) Å) is larger than the sum of the covalent radii (2.24 Å for axial Te–N) [6,7] and longer than that reported for the same interaction in $Te(C_6H_4N_2Ph)(SCN)$ [2.243 Å] [10] and $Te(C_6H_4N_2Ph)Cl$ (2.230 Å) [11], but compares well with the values reported for $Te(C_6H_4N_2Ph)(dmdtc)$ (2.340 Å) [9] and $Te(C_5H_4NPh)(dmdtc)$ (2.354 Å) [1]. The Te–N interaction holds the organic ligand in the almost planar geometry, noted above.

The Te–S(1) bond length (2.569(1) Å, 2.543(1) Å) is in good agreement with the sum of the S and Te axial covalent radii (2.58 Å) [6,7] and with values found in other tellurium(II) complexes containing sulphur ligands, e.g. $Te(C_6H_4N_2Ph)(dmdtc)$ [9], $Te(C_5H_4NPh)(dmdtc)$ [1] and $Te(Et_2NCS_2)_2$ [12], which fall in the range 2.52–2.57 Å. Compared with (2-phenylazophenyl-*C*,*N*′)thiocyanatotellurium(II) (Te–C 2.073 Å, Te–N 2.243 Å and Te–S 2.672 Å) [10], the bonding to the ligand is somewhat weaker and that to the sulphur somewhat stronger.

The Te–S(2) distance (3.222(1) Å, 3.230(1) Å), although within the sum of the Van der Waals radii (4.05 Å) [7] or (3.86 Å) [13], seems to indicate only a weak secondary interaction between these atoms, which is a feature noted in $Te(C_6H_4N_2Ph)(dmdtc)$ (Te...S(2) 3.225 Å) [9].

The approach to the tellurium by a fourth atom, S(2) of the dimethyldithiocarbamate group, could be considered to be a manifestation of the tendency of Te^{II} to achieve a square planar geometry, as has been reported for many Te^{II} complexes. In this compound both the sulphur atoms are essentially coplanar with the tellurium atom and the coordinating C and N atoms of the organic ligand. This situation is akin to that found in dimethyldithiocarbamato(2-phenylazophenyl-*C*,*N*′)tellurium-(II) [9], but in contrast to that in dimethyldithiocarbamato(2-[2-pyridyl]phenyl)tellurium(II) [1], where the dimethyldithiocarbamate group is oriented at an angle of 72.7(3)° to the tellurium-organic ligand plane and there is considered to be no significant interaction between Te and S(2) (Te...S(2) 3.667(1) Å) [1].

As pointed out earlier by Foss et al. [14,15], the *trans* effect of the phenyl group in three coordinate tellurium(II) complexes is pronounced. In our compound we have the typical "T-shape" found for three coordinate tellurium(II) complexes, with the phenyl group at the stem of the "T", and no strong interactions *trans* to the phenyl group. This is consistent with results we described previously [1,2] and with the work of Vikane [16].

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