A novel mixed valence iodide bridged Te(II) - Te(IV)complex featuring diisopropyldithiocarbamate(L) and iodide: $ILTe^{II}(I)Te^{IV}L_2I$

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Abstract

The title compound is a novel mixed ligand and mixed valence complex of tellurium, the crystal structure of which is reported here. The compound crystallizes in the orthorhombic space group, Pca2₁ with four molecules per unit cell, the dimensions of which are a = 15.209(1), b = 20.159(2), c = 12.453(1) Å. The structure was solved by the heavy-atom method and refined by full-matrix least-squares method to a final R = 0.046 and $R_w = 0.046$ for 3011 unique reflections. The structure could be considered as 1:1 adduct of Te^{IV}L₂I₂ and Te^{II}LI (L = diisopropyldithiocarbamate). The two tellurium atoms, Te^{II}[Te(1)] and Te^{IV}[Te(2)] display entirely different coordinations and are

bridged through iodine I(1) in a symmetrical manner. There is a short $Te(1) \cdot \cdot \cdot Te(2)$ contact distance of 3.542(1) Å.

Introduction

Mixed ligand complexes of Te^{II} and Te^{IV} with dithiocarbamates and halogens are rare (Appa Rao *et al.*, 1983; Radha *et al.*, 1986; Schnabel *et al.*, 1979). For the first time a mixed valence and mixed ligand complex of tellurium with the strongly chelating dithiocarbamate as one of the ligands has been prepared. The title compound has many novel features: (i) mixed ligand and mixed valence complex of tellurium; (ii) entirely different coordinations around the heterovalent tellurium atoms; (iii) bridging of the two tellurium atoms by an iodine in a nearly symmetrical manner and (iv) a short $Te^{II} \cdot \cdot \cdot Te^{IV}$ contact. The synthesis and crystal structure of the title compound are reported here.

Experimental

The title compound was synthesized as follows: $0.050 \text{ g} (3.9 \times 10^{-4} \text{ mol})$ of elemental tellurium and 0.088 g of iodine $(3.46 \times 10^{-4} \text{ mol})$ were stirred together in about 25 ml of dichloromethane for 1 hr. To this, a solution of 0.145 g $(1.73 \times 10^{-4} \text{ mol})$ of TeL₄ in about 10 ml of dichloromethane was added and stirred for 3 hr. The small excess of tellurium was filtered out. To the solution, 20 ml of anhydrous ethylacetate was added and on slow evaporation to a small volume (≈ 5 ml) reddish brown plate-like crystals of the title compound were formed. They were recrystallized from a dichloromethane–ethylacetate mixture. Analysis (wt%) found (expected) for Te₂(C₇H₁₄NS₂)₃I₃:

C 21.7 (21.65), H 3.6 (3.63) N 3.5 (3.61) S 16.2 (16.51) Te 21.8 (21.91) I 32.8 (32.68)

The elemental tellurium used was prepared as a fine powder by the reduction of Te^{IV} by hydrazine in 4 *M* HCl medium. The TeL_4 used was prepared by addition of excess diisopropyldithiocarbamate to tellurium dioxide dissolved in 0.25 *M* NaOH, followed by addition of excess 1 *M* acetic acid. TeL_4 was precipitated as an orange yellow solid. It was washed rapidly with water and air dried.

From the stoichiometry of the reactants, the reaction leading to the formation of the title compound could be written as,

$$5\text{Te}^\circ + 6\text{I}_2 + 3\text{Te}^{\text{IV}}\text{L}_4 - 4[\text{Te}\text{L}_2\text{I}_2 \cdot \text{Te}\text{LI}]$$

Crystal Structure of Tellurium

The slight excess of Te^{\circ} was used to make the reaction go to completion. Under the conditions of the experiment, even though excess Te^{\circ} was used, all the Te^{IV} was not reduced to Te^{II} and only the mixed valence complex was realized.

A single crystal of approximate dimensions, $0.05 \times 0.125 \times 0.3$ mm was mounted on glass fiber and centered on an Enraf-Nonius CAD-4 diffractometer. Lattice parameters and their esd's were obtained by least-squares refinement of the setting angles of 23 carefully centered reflections in the range $40^{\circ} \le 2\theta \le$ 50° .

Crystallographic data are as follows: Te₂(C₆H₁₄NCS₂)₃I₃, $M_r = 1164.84$, orthorhombic, space group Pca2₁(No. 29), a = 15.209(1), b = 20.159(2), c = 12.453(1) Å, U = 3818.06 Å³, Z = 4, $D_x = 2.026$ mg⁻³, λ (Cu K_{α}) = 1.5418 Å, μ (Cu K_{α}) = 33.47 mm⁻¹, F(000) = 2191.95, T = 293 K.

Intensity data were collected by the $\omega - 2\theta$ scan technique for $2\theta < 130^{\circ}$ (index range: $h -7 \rightarrow 18, k -9 \rightarrow 24, 1 -15 \rightarrow 13$) with graphite monochromated Cu K_{α} radiation. Two standard reflections were monitored every hour as a check on crystal and instrument stability, and showed no significant variation in intensity during the data collection. Unique reflections (3011) with $I > 2.5\sigma(I)$ considered observed. The intensity data were corrected for Lorentz and polarization effects. Absorption correction was applied using the method of Walker and Stuart (1983) and the maximum and minimum transmission factors were 0.67 and 2.15, respectively.

The structure was solved by the heavy-atom method. Te and I positions were obtained from the Patterson map and the successive Fourier maps based on Te and I positions gave the location of all nonhydrogen atoms. The positions of nonhydrogen atoms were refined allowing for anisotropic thermal motion by full-matrix least-squares method using SHELX 76 (Sheldrick, 1976). All the hydrogen atom positions were fixed geometrically since they could not be located from the final difference Fourier maps and were not refined. Refinement was terminated when the maximum shift per esd for any parameter was below $0.044 \cdot 315$ parameters refined and the reflection to parameter ratio was 9.56. Residuals at convergence were R = 0.046 and $R_w = 0.046$ for 3011 unique reflections. Individual weights were ascribed according to the scheme w = k/k $(\sigma^2(F_0) + g|F_0|^2)$, where the final k and g values were 2.4208 and 0.00064, respectively. The final difference Fourier map showed no unusual features with the largest peak maximum being 1.28 $e^{A^{-3}}$ which is in proximity to tellurium and has no chemical significance. Atomic scattering factors for nonhydrogen atoms were taken from Cromer and Mann (1968) and for hydrogen atoms were taken from Stewart et al. (1965). Anomalous dispersion correction factors were from Cromer and Liberman (1970).

The final values of the positional parameters and equivalent isotropic thermal parameters for nonhydrogen atoms are given in Table 1. The bond lengths are bond angles involving the nonhydrogen atoms are shown in Table 2.

Atom	x	у	z	$U_{ m eq}$
Te(1)	-0.0059(1)	0.3210(1)	0.3718	355(6)
Te(2)	0.1476(1)	0.1991(1)	0.4546(2)	326(5)
I(1)	0.0061(1)	0.1735(1)	0.2507(2)	530(8)
I(2)	0.0885(1)	0.4523(1)	0.3641(2)	564(8)
I(3)	0.0559(1)	0.1717(1)	0.6607(2)	667(10)
S(1)	-0.0845(3)	0.3835(2)	0.5093(5)	42(2)
S(2)	-0.1276(3)	0.2490(2)	0.4522(6)	43(2)
S(3)	0.1825(3)	0.0831(2)	0.3669(6)	54(3)
S(4)	0.2835(3)	0.1516(2)	0.5329(5)	49(3)
S(5)	0.2184(3)	0.3034(2)	0.5375(4)	38(2)
S(6)	0.2402(3)	0.2589(2)	0.3139(5)	43(3)
C(1)	-0.1535(11)	0.3179(7)	0.5324(15)	33(9)
C(2)	-0.2814(13)	0.2628(9)	0.6205(19)	50(12)
C(3)	-0.3349(14)	0.2440(12)	0.5228(24)	68(16)
C(4)	-0.2365(17)	0.2047(10)	0.6743(22)	67(15)
C(5)	-0.2406(15)	0.3835(9)	0.6563(21)	56(13)
C(6)	-0.2373(17)	0.3761(13)	0.7734(21)	67(16)
C(7)	-0.3291(17)	0.4082(12)	0.6179(28)	84(19)
C(8)	0.2769(9)	0.3102(7)	0.4198(15)	29(9)
C(9)	0.3825(14)	0.3995(11)	0.4938(18)	51(13)
C(10)	0.3186(13)	0.4444(8)	0.5346(23)	58(13)
C(11)	0.4224(14)	0.3518(13)	0.5825(22)	64(15)
C(12)	0.3882(13)	0.3547(11)	0.2967(20)	51(13)
C(13)	0.4851(14)	0.3418(14)	0.3102(22)	69(16)
C(14)	0.3706(18)	0.4229(15)	0.2503(28)	88(21)
C(15)	0.2737(11)	0.0816(7)	0.4469(17)	35(9)
C(16)	0.4121(15)	0.0441(11)	0.5206(25)	69(15)
C(17)	0.4963(18)	0.0511(16)	0.4638(36)	104(24)
C(18)	0.4130(22)	-0.0111(16)	0.6066(30)	109(26)
C(19)	0.3345(15)	-0.0247(9)	0.3757(25)	61(13)
C(20)	0.2545(22)	-0.0688(9)	0.4040(27)	86(18)
C(21)	0.3365(16)	-0.0071(12)	0.2602(22)	66(16)
N(1)	-0.2205(9)	0.3193(7)	0.6015(15)	45(9)
N(2)	0.3431(10)	0.3508(7)	0.4052(13)	38(8)
N(3)	0.3352(10)	0.0378(8)	0.4482(17)	48(10)

Table 1. Fractional atomic coordinates of non-hydrogen atoms and their equivalent isotropic thermal parameters ($Å^2$, $\times 10^4$ for Te and I; $\times 10^3$ for the rest) with esd's in parentheses^{*a*}

 ${}^{a}U_{eq} = \frac{1}{3} \sum_{i=1}^{3} U_{ii}$

Results and discussion

A perspective view of the structure is depicted along with the atom numbering scheme in Fig. 1 (Motherwell, 1978). There are two telluriums with entirely different coordination geometries as shown in Fig. 2. The coordination geometries enabled the assignment of the oxidation states of the tellurium atoms. The title compound can be considered as an 1:1 adduct of $Te^{IV}L_2I_2$ and $Te^{II}LI$ (L = diisopropyldithiocarbamate) with the tellurium atoms $Te^{II}[Te(1)]$ and

Crystal Structure of Tellurium

Te(1) = I(1)	3.338(2)	Te(1) - I(2)	3.013(2)
Te(1) = S(1)	2.440(5)	Te(1) - S(2)	2.556(5)
Te(2) - I(1)	3.368(2)	Te(2)-I(3)	2.973(3)
Te(2) - S(3)	2.635(5)	Te(2) - S(4)	2.478(5)
Te(2) - S(5)	2.578(5)	Te(2) - S(6)	2.552(6)
S(1) = C(1)	1.713(16)	S(2) - C(1)	1.756(17)
S(3) - C(15)	1.708(19)	S(4) - C(15)	1.779(18)
S(5) - C(8)	1.721(18)	S(6)-C(8)	1.766(17)
C(1) - N(1)	1.334(24)	C(2) - C(3)	1.512(35)
C(2) - C(4)	1.512(30)	C(2) = N(1)	1.488(24)
C(5) - C(6)	1.466(37)	C(5) - C(7)	1.513(35)
C(5) - N(1)	1.494(25)	C(8) - N(2)	1.310(20)
C(9) - C(10)	1.502(29)	C(9) - C(11)	1.516(35)
C(9) - N(2)	1.523(27)	C(12) - C(13)	1.506(29)
C(12) - C(14)	1.514(39)	C(12) - N(2)	1 517(29)
C(15) = N(3)	1.286(21)	C(16) - C(17)	1.077(29) 1.470(40)
C(16) - C(18)	1 545(44)	C(16) = N(3)	1 482(31)
C(19) - C(20)	1 548(36)	C(19) - C(21)	1.482(31) 1.482(41)
C(19) - N(3)	1.551(29)	0(1)) 0(21)	1.402(41)
C(1)) II(3)	1.551(27)		
I(1) = Te(1) = I(2)	137.9(1)	I(1) - Te(1) - S(1)	143.5(1)
I(1) - Te(1) - S(2)	73.2(1)	I(2) - Te(1) - S(1)	78 6(1)
I(2) - Te(1) - S(2)	148.9(1)	S(1) - Te(1) - S(2)	70 3(2)
I(1) - Te(2) - I(3)	108.8(1)	I(1) - Te(2) - S(3)	71.4(1)
I(1) - Te(2) - S(4)	140 4(1)	I(1) - Te(2) - S(5)	133.9(1)
I(1) - Te(2) - S(6)	84.7(1)	I(1) - Te(2) - S(3)	106.7(2)
I(3) - Te(2) - S(4)	88 8(2)	I(3) - Te(2) - S(5)	90.1(1)
I(3) - Te(2) - S(6)	160.0(1)	S(3) - Te(2) - S(4)	69.6(2)
S(3) - Te(2) - S(5)	143.7(1)	S(3) - Te(2) - S(6)	91.4(2)
S(4) - Te(2) - S(5)	79.0(2)	S(4) - Te(2) - S(6)	89 5(2)
S(5) - Te(2) - S(6)	70.0(2)	Te(1) - I(1) - Te(2)	63.8(0)
Te(1) = S(1) = C(1)	91.1(6)	Te(1) = S(2) = C(1)	86.3(6)
Te(2) = S(3) = C(15)	86.4(6)	Te(2) = S(4) = C(15)	90.0(6)
Te(2) - S(5) - C(8)	86.6(5)	Te(2) = S(6) = C(8)	86 5(6)
S(1) - C(1) - S(2)	112 2(10)	S(1) - C(1) - N(1)	124 1(13)
S(2) - C(1) - N(1)	123 7(12)	C(3) - C(2) - C(4)	113 9(18)
C(3) - C(2) - N(1)	113 5(19)	C(4) - C(2) - N(1)	112.9(16) 112.4(16)
C(6) - C(5) - C(7)	112.2(22)	C(6) - C(5) - N(1)	112.4(10) 111.0(18)
C(7) - C(5) - N(1)	108.8(19)	S(5) - C(8) - S(6)	115 2(8)
S(5) - C(8) - N(2)	124 5(14)	S(6) - C(8) - N(2)	120.3(14)
C(10) - C(9) - C(11)	113 1(20)	$\Gamma(10) - \Gamma(9) - N(2)$	1120.3(17) 112(2(17))
C(11) - C(9) - N(2)	111 8(18)	C(13) - C(12) - C(14)	111.9(20)
C(13) - C(12) - N(2)	109 5(19)	C(14) - C(12) - N(2)	107.9(19)
S(3) - C(15) - S(4)	113.9(8)	S(3) = C(15) = N(3)	127 6(15)
S(4) - C(15) - N(3)	118.4(15)	C(17) - C(16) - C(18)	113 3(23)
C(17) - C(16) - N(3)	113 8(27)	C(18) - C(16) - N(3)	111 5(20)
C(20) - C(19) - C(21)	112.0(23)	C(20) - C(19) - N(3)	109.8(20)
C(21) - C(19) - N(3)	111.7(17)	C(1) = N(1) = C(2)	124.2(15)
C(1) = N(1) = C(5)	118.0(15)	C(2) - N(1) - C(5)	117.6(16)
C(8) - N(2) - C(9)	123.7(16)	C(8) - N(2) - C(12)	120,3(16)
C(9) = N(2) = C(12)	116.0(15)	C(15) - N(3) - C(16)	121.5(18)
C(15) = N(3) = C(19)	123.1(17)	C(16) - N(3) - C(19)	115.4(16)
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 Table 2. Bond lengths (Å) and bond angles (deg) involving non-hydrogen atoms with esd's in parentheses

Ganesh et al.



Fig. 1. Plot of the molecule along with the atom numbering scheme.

 $Te^{IV}[Te(2)]$ bridged by iodine, I(1). We have been able to prepare $Te^{IV}L_2I_2$ as an independent compound but our attempts to prepare $Te^{II}LI$ as an independent compound have so far been unsuccessful. The packing of the molecules in the unit cell is shown in Fig. 3 and the lattice stabilization is ensured by van der Waal's interactions.



Fig. 2. Coordination of Te(1) and Te(2).



Fig. 3. Packing of the molecules in the unit cell.

The Te^{II} coordination

Te(1) is coordinated to two sulphurs, S(1) and S(2) of the diisopropyldithiocarbamate (dtc) ligand in an unequal bidentate manner and to two iodines, I(1) and I(2). The coordination around Te(1) is characteristically planar trapezoidal (Rout et al., 1983) with TeS(1)S(2)I(1)I(2) forming a mean plane with the maximum deviation being 0.023(5) Å. The two lone pairs of electrons of Te(1) lie one above and below the TeS(1)S(2)I(1)I(2) plane. The average Te(1) – S bond (2.498(5) Å) in the title compound is shorter than the average Te-S bond (2.525(8) Å) observed for similar Te in tris[bis(2-hydroxyethyl)dithiocarbamate]-haloditellurium(II)[A] (Radha et al., 1986) and very much shorter than the average Te-S bond (2.677(3) Å) observed in bis(dipropyldithiocarbomato)-tellurium(II)[B] (Ganesh et al., 1988). The shortening of Te-S(1) and Te-S(2) bonds in the ligand may be due to the weaker bonding to Te of I(1) and I(2), respectively, trans to the sulfurs. The S(1) - Te(1) - S(2) angle (70.3(2)°) is equal to the S-Te-S angle (70.4(3)°) observed in B. Te(1)-I(1) and Te(1)-I(2) distances are longer than the sum of the covalent radii of Te and I (2.60 Å) (Alcock, 1972). Te(1)-I(1) distance is longer than Te(1)-I(2) distance since I(1) participates in bridging Te(1) and Te(2).

The Te^{IV} coordination

Te(2) is essentially six coordinated to four sulfurs S(3), S(4), S(5), and S(6) of the two dtc ligands and to two iodines I(1) and I(3), but can be consid-

ered to be as seven coordinated taking Te(1) into consideration. Taking the latter coordination, the coordination geometry around Te(2) can be described as a distorted pentagonal-bipyramidal geometry with S(3), S(4), S(5), I(1), and Te(1) in the equatorial girdle and I(3) and S(6) nearly in the axial line. The I(3)-Te(2)-S(6) angle is 160.0(1)°. Atoms Te(2), Te(1), S(3), S(4), S(5), and I(1) form a distorted plane, maximum deviation of any atom from the mean plane being 0.287(2) Å. The pentagonal-bipyramidal coordination geometry around Te(2) agrees with the geometry predicted by Kepert (1975) from minimum energy calculations for the structures of the type $M(bidentate)_2(unidentate)_3$. For Te(2), which is six coordinated to 4S and 2I, the active lone pair will be lying between I(1) and S(5). Generally in the Te^{IV} dithiocarbamate complexes, the dtc ligand is attached to Te in an unequal bidentate manner. However, interestingly, one of the dtc groups in the present structure [S(5), S(6)] forms nearly equal Te-S bonds. The average Te(2)-S bonds (2.561(5) Å) in the title compound is shorter than 2.640(7) Å observed in bis[bis(2-hydroxyethyl)dithiocarbamato]diiodotellurium(IV)[C] (Appa Rao et Å observe in thiocyanato tris[bis(2-hydroxyal., 1983). 2.656(2)ethyl)dithiocarbamato]tellurium(IV)[D] (Rout et al., 1984a) and 2.738(4) Å observed in tetrakis[bis(2-hydroxyethyl)dithiocarbamato]tellurium(IV)[E] (Rout et al., 1984b) but close to 2.59 Å, the sum of octahedral radius of Te and covalent radius of sulphur which indicates a strong bonding between Te(2) and S. It is interesting to note here the observation of Appa Rao (1981) and Rout (1984) that Te-S bond length increases with the increasing number of dtc ligands. The average intraligand S - Te(2) - S bond angle $(69.8(2)^{\circ})$ is close to the average S-Te-S bond angle $(67.4(2)^{\circ})$ observed in C but greater than the average S-Te-S bond angle (65.1(2)°) observed in E. As in the case of Te(1), the Te(2)-I(1) distance is longer than the Te(2)-I(3) distance.

$Te \cdot \cdot \cdot Te$ interactions

The $\text{Te}^{II} \cdots \text{Te}^{IV}$ contact distance (3.542(1) Å) observed in the title compound is greater than $\text{Te}^{II} \cdots \text{Te}^{II}$ contact distance of 3.221(3) Å observed in A and is comparable with the interchain $\text{Te} \cdots \text{Te}$ distance in metallic tellurium (3.55 Å) (Wyckoff, 1960). The Te(1)-Te(2) axis makes an angle of 57.9° with the Te(1)S(2)I(1)I(2) plane. Te(1) and Te(2) are bridged by iodine, I(1) in a nearly symmetrical manner Te(1) - I(1) = 3.338(2); Te(2) - I(1) =3.368(2) Å with a bridging angle of 63.8(1)°. This low angle bespeaks of a close metal-metal interaction analogous to those reported for similar systems (Howard *et al.*, 1988). There are no $\text{I} \cdots \text{I}$ interactions in the structure unlike that observed in C.

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Structure factor data have been deposited with the British Library, Boston Spa, Wetherby, West Yorkshire, UK, as supplementary publication No. 63101 (20 pages).