The Crystal and Molecular Structure of an Eight-coordinated Tellurium(IV) Complex

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Tetrakis(4-morpholinecarbodithioato)tellurium-(IV), [Te(OC$_4$H$_8$N.CS$_2$)$_4$], crystallizes from benzene-ethanol mixtures with three benzene molecules per molecule of complex. The yellow to orange crystals belong to the space group $P2_1/c$, with $a=15.445(4)$ Å, $b=13.565(4)$ Å, $c=26.591(10)$ Å and $\beta=122.23(4)°$. With four formula units, [Te(OC$_4$H$_8$N.CS$_2$)$_4$]3C$_6$H$_6$, in the cell, the density is calc. 1.43, found 1.45 g/cm^3.

The structure analysis is based on 2721 intensities above background, collected with a Siemens AED-1 diffractometer using MoKα radiation. Patterson and Fourier syntheses were used to solve the structure, and full-matrix least squares refinement has given a conventional R-value of 0.094.

In the complex molecule, the central tellurium atom is bonded to all eight sulfur atoms in a slightly distorted dodecahedral D_{2d} configuration. The Te$-$S bond lengths vary between 2.672 and 2.824 Å, the average being 2.737 Å.

During the study of compounds of divalent selenium and tellurium with bidentate dithio and related ligands, it was generally found that the ligands upon reaction with Se(IV) and Te(IV) reduced the elements to the divalent state.[1,2] Thus the reaction could be used to prepare complexes of divalent selenium and tellurium. The other part of the redox process taking place is the oxidation of two ligands to a disulfide molecule.[1,3] With diethyldithiocarbamate as ligand, the tetravalent selenium and tellurium complexes are initially formed,[4,5] and the tellurium(IV) complex is stable enough to be isolated in the crystalline state,[6,7] before conversion to divalent complex and disulfide takes place. The general reaction between tetravalent element and bidentate dithio ligand is then (L is ligand, L$_2$ is disulfide)[7]:

$$M(IV) + 4L^- \rightleftharpoons ML_4 \rightleftharpoons ML_2 + L_2$$
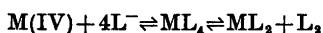
Only with M=Te and L=dialkyldithiocarbamate has ML$_4$ been stable enough to be isolated. The structure of both ML$_4$, ML$_2$ and L$_2$ are known for L=diethyldithiocarbamate and M=Te,[7-9] and there are several common features in the manner in which the ligands are coordinated to the central atom in ML$_4$ and ML$_2$. In ML$_2$ the TeS$_4$ coordination is trapezoid planar, in ML$_4$ the TeS$_8$ coordination is dodecahedral, and may be described by two planar TeS$_4$ trapezoids at right angles to each other fused together at the tellurium atom.[7]

Unlike tetrakis(diethyldithiocarbamato)tellurium(IV), [Te(dtc)$_4$], tetrakis(4-morpholine-carbodithioato)tellurium(IV), [Te(mtc)$_4$], which is also a dithiocarbamate complex, is remarkably resistant to conversion to divalent complex and disulfide when heated in solution.

This structure investigation was partly undertaken to see if the difference in behaviour of the two complexes is due to some structural feature, and partly to investigate further the stereochemical role of the lone pair of electrons in highly coordinated tellurium(IV) compounds.

A lone pair of electrons has so far been shown to be stereochemically inert in complexes of several ions in the lower right hand corner of the periodic table with a $(n-1)d^{10}ns^2$ electron configuration. Examples are octahedral complexes of Se(IV), Te(IV), Sb(III), Bi(III), Pb(II).[10-14] Also for [Te(dtc)$_4$],[7] the lone pair is found to be stereochemically inert. Several explanations have been given for this behaviour, one delocalizing the lone pair mainly on the ligands,[15,16] another using the three-center

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four-electron description,[17] and a third explaining it in terms of steric repulsions.[18,19]

EXPERIMENTAL

The preparation of crystals of tetrakis(4-morpholinecarbodithioato)tellurium(IV) with three benzene molecules of crystallization per molecule of complex, [Te(mtc)$_4$].3C$_6$H$_6$, is reported elsewhere.[20] The crystals consisted of flat yellow to orange plates and prisms. Tiny red prisms were also seen adhering to nearly all of the larger crystals; these were probably crystals of the corresponding divalent complex, [Te(mtc)$_2$].[21] Upon standing, the crystals slowly become covered by a yellow powder.

For recording of intensity data, a Siemens AED-1 tape-controlled single crystal diffractometer and MoKα radiation were used. A small crystal, with dimensions $0.18 \times 0.13 \times 0.09$ mm^3, was mounted along the c axis. After measuring the angles θ, χ, and ψ for three non-coplanar reciprocal vectors, approximate setting angles for all reflections were calculated.

Accurate cell dimensions were based on measurements of accurate setting angles for 20 high order reflections, and determined by least squares methods. They are $a = 15.445(4)$ Å, $b = 13.565(4)$ Å, $c = 26.591(10)$ Å and $\beta = 122.23(4)°$. There are four formula units in the cell. The observed and calculated densities are 1.45 and 1.43 g/cm^3, respectively. Based on systematic extinctions $h0l$ for $l = 2n+1$ and $0k0$ for $k = 2n+1$, the space group is $P2_1/c$.

After determination of accurate setting angles, intensity data were collected using a scintillation counter and $\theta - 2\theta$ scan technique. The scan speed was 2.50° per min, with automatic setting of greater speed for strong reflections. Attenuation filters were used to avoid counting losses. The reflections were scanned between $\theta_1 = \theta - 0.40°$ and $\theta_2 = \theta + 0.40°$, where θ is the Bragg angle for the α_1 peak.

The scan was performed by going from θ to θ_1, then from θ_1 to θ_2 and finally from θ_2 to θ. The intensities for all three scans and their sum I_t were recorded. Likewise, background was measured for one half the total scan time at both θ_1 and θ_2, and the respective intensities and their sum I_b were recorded. The net intensity for a reflection, I_N, was put equal to $I_t - I_b$.

Two reference reflections were measured at intervals of 50 reflections and the intensity variations for these reflections were used to scale the net intensities of the recorded reflections. The standard deviation in net intensity is defined as the square root of the sum of I_b and I_t. Reflections with net intensities less than twice the standard deviation were regarded as unobserved and assigned intensities equal to this lower intensity limit. Out of 5800 measured reflections only 2721 were observed. This is

Table 1. Final coordinates for the atoms in the asymmetric unit in fractions of cell edges.

	x	y	z
Te	0.11791(11)	0.23045(9)	0.15583(6)
S1	0.2399(5)	0.0589(4)	0.1981(2)
S2	0.0877(5)	0.1145(4)	0.2274(3)
S3	0.2868(5)	0.3074(4)	0.2501(2)
S4	0.0814(5)	0.3732(4)	0.2158(2)
S5	0.0866(5)	0.3879(4)	0.0878(2)
S6	0.2457(4)	0.2443(4)	0.1101(2)
S7	−0.0909(4)	0.2434(4)	0.1004(2)
S8	0.0111(5)	0.1122(4)	0.0600(2)
O1	0.3178(14)	−0.1460(13)	0.3804(7)
O2	0.3397(14)	0.6155(12)	0.3766(7)
O3	0.3004(14)	0.5553(12)	0.0142(7)
O4A	−0.3762(25)	0.0635(24)	−0.0920(13)
O4B	−0.3684(30)	0.0172(25)	−0.0658(16)
N1	0.2163(14)	−0.0347(13)	0.2771(8)
N2	0.2549(13)	0.4487(12)	0.3063(7)
N3	0.2174(15)	0.4144(13)	0.0537(8)
N4	−0.1909(17)	0.1205(15)	0.0092(9)
C11	0.1865(15)	0.0391(14)	0.2387(8)
C21	0.1699(19)	−0.0533(16)	0.3118(10)
C31	0.2557(20)	−0.0669(18)	0.3377(11)
C41	0.3673(21)	−0.1283(17)	0.3507(12)
C51	0.2858(19)	−0.1147(18)	0.2813(10)
C12	0.2112(16)	0.3826(13)	0.2623(8)
C22	0.3680(18)	0.4560(14)	0.3529(9)
C32	0.3980(21)	0.5652(18)	0.3577(11)
C42	0.2284(19)	0.6168(17)	0.3290(10)
C52	0.1876(18)	0.5129(16)	0.3217(9)
C13	0.1841(16)	0.3555(14)	0.0804(8)
C23	0.2914(22)	0.3833(19)	0.0361(11)
C33	0.3648(23)	0.4723(22)	0.0476(12)
C43	0.2396(23)	0.5888(20)	0.0373(12)
C53	0.1600(18)	0.5083(16)	0.0232(9)
C14	−0.0987(17)	0.1551(14)	0.0520(9)
C24	−0.2859(23)	0.1599(19)	0.0008(11)
C34A	−0.3689(35)	0.1475(32)	−0.0580(20)
C34B	−0.2674(47)	−0.0128(37)	−0.0492(23)
C44A	−0.2839(40)	0.0404(33)	−0.0877(20)
C44B	−0.3440(34)	0.0785(32)	−0.0093(18)
C54	−0.1953(30)	0.0464(27)	−0.0024(16)
C101	−0.0030(18)	0.1831(17)	0.3346(10)
C102	0.0003(19)	0.2781(22)	0.3234(11)
C103	−0.0002(20)	0.3530(19)	0.3619(11)
C104	−0.0067(19)	0.3203(18)	0.4123(10)
C105	−0.0040(21)	0.2224(24)	0.4236(12)
C106	−0.0047(18)	0.1491(16)	0.3832(10)
C201	0.2890(20)	0.2319(21)	0.3901(11)
C202	0.2911(21)	0.2886(20)	0.4348(12)
C203	0.3865(24)	0.3005(19)	0.4911(12)
C204	0.4711(19)	0.2515(19)	0.4983(10)
C205	0.4745(22)	0.1940(20)	0.4557(13)
C206	0.3755(23)	0.1853(18)	0.4003(11)
C301	0.5328(29)	0.0749(29)	0.2750(14)
C302	0.5287(28)	0.1806(30)	0.2762(14)
C303	0.6140(30)	0.2454(26)	0.2954(14)
C304	0.7058(22)	0.1942(22)	0.3141(11)
C305	0.7026(22)	0.0969(23)	0.3085(11)
C306	0.6235(29)	0.0342(22)	0.2902(13)

Table 2. Components of atomic vibration tensors, $U \times 10^3$, in Å^2 with standard deviations, referred to crystallographic axes. For Te and S the expression is $\exp\{-2\pi^2(h^2a^{-2}U_{11}+k^2b^{-2}U_{22}+l^2c^{-2}U_{33}+2hka^{-1}b^{-1}U_{12}+2klb^{-1}c^{-1}U_{23}+2hla^{-1}c^{-1}U_{13})\}$. For O, N, and C, the expression is $\exp\{-8\pi^2\bar{U}\times(\sin^2\theta/\lambda^2)\}$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Te	51.9(1.0)	40.0(0.7)	50.1(0.8)	5.7(0.9)	1.2(0.9)	30.9(0.7)
S1	74.3(5.0)	59.1(3.8)	76.1(4.2)	16.2(3.5)	12.2(3.2)	51.6(4.0)
S2	73.5(5.4)	54.7(3.7)	68.7(4.1)	11.4(3.5)	13.5(3.2)	48.0(4.0)
S3	64.4(4.8)	60.7(3.8)	79.5(4.3)	8.2(3.4)	−20.4(3.2)	37.8(3.9)
S4	65.1(5.2)	51.5(3.7)	64.4(4.1)	6.4(3.5)	−6.6(3.1)	37.1(3.9)
S5	57.1(4.6)	56.2(3.7)	81.5(4.4)	18.8(3.5)	20.8(3.4)	45.1(3.9)
S6	79.0(4.6)	56.5(4.1)	87.1(4.0)	23.3(3.7)	22.2(3.4)	56.4(3.7)
S7	63.2(4.5)	53.3(3.9)	65.8(3.4)	−2.4(3.5)	−9.3(2.9)	37.2(3.4)
S8	52.1(4.5)	74.2(4.2)	61.4(3.9)	7.6(3.7)	−15.6(3.4)	28.8(3.6)

	U		U		U		U
O1	113.9(6.3)	C51	93.1(8.2)	C34A	67.6(14.4)	C203	112.4(10.0)
O2	105.6(5.8)	C12	49.7(5.8)	C34B	86.1(17.2)	C204	87.7(8.1)
O3	105.3(6.0)	C22	66.1(6.7)	C44A	67.5(14.7)	C205	109.9(10.1)
O4A	74.5(10.0)	C32	97.2(8.7)	C44B	70.1(13.7)	C206	102.9(9.1)
O4B	72.1(12.2)	C42	88.3(8.0)	C54	148.6(14.1)	C301	166.1(13.8)
N1	72.4(5.6)	C52	75.3(7.5)	C101	88:3(7.8)	C302	169.7(14.1)
N2	61.7(5.1)	C13	54.4(6.1)	C102	116.6(8.9)	C303	162.6(12.5)
N3	76.2(5.9)	C23	113.8(9.6)	C103	95.0(9.1)	C304	109.3(9.5)
N4	92.8(6.6)	C33	125.4(10.8)	C104	90.9(8.2)	C305	110.6(9.7)
C11	50.5(5.9)	C43	114.8(10.0)	C105	126.6(10.1)	C306	130.8(11.3)
C21	86.4(8.2)	C53	74.6(7.3)	C106	86.7(7.6)		
C31	91.7(8.5)	C14	60.3(6.4)	C201	99.6(8.4)		
C41	105.1(9.1)	C24	102.8(9.1)	C202	109.1(9.4)		

Table 3. Dodecahedral parameters for some complexes with approximate D_{2d} symmetry. The unit of length for a, b, g, and m is in each case equal to the average central atom to ligand bond length.

Compound	ϕ_A	ϕ_B	MA/MB	a	b	g	m
[Te(mtc)$_4$]	37.4	77.8°	1.04	1.24	1.42	1.29	1.07
[Te(dtc)$_4$][7]	35.0	79.9	1.02	1.16	1.42	1.31	1.07
[Ti(dtc)$_4$][27]	35.1	77.5	1.03	1.17	1.42	1.29	1.11
[V(dta)$_4$][28]	35.4	77.0	1.02	1.17	1.44	1.27	1.11
"Best" values[25]	35.2	73.5	1.03	1.17	1.49	1.24	1.17

partly due to a yellow powder appearing on the surface of the crystal during exposure. The powder probably consists of crystal material from which the benzene molecules have escaped. This effect is probably also the cause of the reduction in the net intensities of the standard reflections with about 30 % during the data collection.

STRUCTURE ANALYSIS

Three-dimensional Patterson and Fourier syntheses revealed the positions of all non-hydrogen atoms in the asymmetric unit, except those of oxygen and two of its neighbour carbon atoms in one of the morpholyl groups.

This part of the ring was later found to be disordered.

Full-matrix least squares refinement was then started using a program (BDLS) which minimizes the expression $r = \sum W(|F_o| - K|F_c|)^2$. Here K is a scale factor and W, the weight of a reflection, is the inverse of the variance of F_o: $\sigma^2(F_o) = F_o^2\{I_t + I_b + k^2(I_t - I_b)^2\}/4(I_t - I_b)^2$, where k may be interpreted as the relative standard deviation in the scaling curve based on the variation in the net intensities of the reference reflections.

Non-observed reflections with $K|F_c|$ larger than the observable limit, were included in the refinement with F_o put equal to the limit.

Based on anisotropic temperature factors for sulfur and tellurium and isotropic temperature factors for oxygen, nitrogen and carbon atoms, the factor $R = (||F_o| - |F_c||)/\sum|F_o|$ converged to a final value of 0.094. Hydrogen atoms were excluded from the calculations and in the morpholyl group with disorder, the ring was given two orientations, A and B, corresponding to a rotation of 180° around the N4—C14 bond and sp^3 hybridization on N4. The disordered atoms in the two configurations were given extra indices A and B and occupancy factors equal to 0.5. A final difference map revealed no spurious peaks.

In the third benzene ring, the temperature factors are very high, especially for the atoms C301, C302, C303. This may be due to the fact that these atoms make very few van der Waals contacts (Table 7); also it could perhaps indicate that not all such benzene positions are occupied.

Table 4. Bond lengths with standard deviations, in Å.

Te—S1	2.824(6)	S7—C14	1.72(2)
Te—S2	2.694(8)	S8—C14	1.68(3)
Te—S3	2.684(5)	C11—N1	1.33(3)
Te—S4	2.752(7)	C12—N2	1.34(2)
Te—S5	2.672(6)	C13—N3	1.34(3)
Te—S6	2.824(8)	C14—N4	1.36(3)
Te—S7	2.744(6)	N1—C21	1.46(4)
Te—S8	2.702(5)	N1—C51	1.49(3)
S1—C11	1.69(3)	N2—C22	1.51(3)
S2—C11	1.73(2)	N2—C52	1.57(4)
S3—C12	1.71(3)	N3—C23	1.51(5)
S4—C12	1.71(2)	N3—C53	1.52(3)
S5—C13	1.68(3)	N4—C24	1.46(4)
S6—C13	1.73(2)	N4—C54	1.47(5)

Table 5. Bond angles with standard deviations, in degrees.

S1—Te—S2	64.41(23)
S3—Te—S4	65.34(20)
S5—Te—S6	64.56(20)
S7—Te—S8	65.16(20)
S1—Te—S6	75.78(21)
S4—Te—S7	73.82(18)
S2—Te—S5	155.27(23)
S3—Te—S8	155.75(23)
Te—S1—C11	86.3(7)
Te—S2—C11	89.9(8)
Te—S3—C12	89.3(6)
Te—S4—C12	87.0(8)
Te—S5—C13	91.2(7)
Te—S6—C13	85.1(10)
Te—S7—C14	86.8(8)
Te—S8—C14	88.9(7)
S1—C11—N1	121.6(1.7)
S2—C11—N1	119.5(1.8)
S3—C12—N2	119.3(1.5)
S4—C12—N2	122.2(1.5)
S5—C13—N3	121.9(1.5)
S6—C13—N3	119.2(1.6)
S7—C14—N4	119.0(1.8)
S8—C14—N4	121.8(1.7)
S1—C11—S2	118.8(1.0)
S3—C12—S4	118.4(1.0)
S5—C13—S6	118.9(1.2)
S7—C14—S8	119.1(1.0)
C11—N1—C21	122.1(1.9)
C11—N1—C51	123.2(2.2)
C21—N1—C51	113.8(1.9)
C12—N2—C22	125.8(1.7)
C12—N2—C52	120.4(1.6)
C22—N2—C52	112.7(1.5)
C13—N3—C23	124.5(1.8)
C13—N3—C53	120.3(2.0)
C23—N3—C53	113.1(2.0)
C14—N4—C24	121.9(2.0)
C14—N4—C54	118.1(2.4)
C24—N4—C54	119.8(2.1)

Table 6. Some non-bonded S—S distances (Å) in the Te(mtc)₄ molecule.

S1—S2	2.943(12)	S6—S8	3.600(9)
S3—S4	2.935(10)	S4—S2	3.520(8)
S5—S6	2.937(9)	S4—S5	3.454(11)
S1—S8	2.933(10)	S7—S2	3.484(7)
S1—S6	3.468(9)	S7—S5	3.528(10)
S4—S7	3.301(7)	S5—S3	3.892(7)
S1—S3	3.568(8)	S5—S8	3.869(8)
S1—S8	3.557(7)	S3—S2	3.833(9)
S6—S3	3.531(10)	S8—S2	3.948(9)

Table 7. Intermolecular distances less than 4.0 Å. The left column represents distances from an atom in the original molecule (Table 1) to an atom in a molecule whose transformation from the original one is listed in the next column.

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C101— S2	x	y	z	3.90(3)
— C201	x	y	z	3.98(4)
— C42	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.96(3)
C102— S4	x	y	z	3.90(4)
— C201	x	y	z	3.87(4)
— C202	x	y	z	3.84(4)
— N1	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.90(3)
— C21	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.87(3)
C103— C202	x	y	z	3.93(4)
— C11	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.69(3)
— N1	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.74(3)
C104— S8	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.90(3)
C105— C304	$-1+x$	y	z	3.85(4)
— C13	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.74(3)
— N3	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.81(3)
C106— C304	$-1+x$	y	z	3.87(4)
— C305	$-1+x$	y	z	3.91(4)
— S5	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.97(3)
— C53	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.85(3)
C201— S3	x	y	z	3.85(3)
— C12	x	y	z	3.58(3)
— N2	x	y	z	3.55(3)
— C22	x	y	z	3.60(4)
C202— N2	x	y	z	3.83(4)
— C22	x	y	z	3.75(4)
— C52	x	y	z	3.97(3)
— C23	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.56(5)
C203— O4B	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.64(5)
— C44B	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.90(5)
— C34B	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.90(8)
— O2	$1-x$	$1-y$	$1-z$	3.96(3)
— C23	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.42(5)
C204— C41	$1-x$	$-y$	$1-z$	3.80(3)
— O1	$1-x$	$-y$	$1-z$	3.44(3)
— O2	$1-x$	$1-y$	$1-z$	3.54(3)
— C23	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.88(5)
— C33	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.99(5)
— C24	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.91(5)
— C34A	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.76(7)
— C44B	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.76(6)
C205— C33	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.93(5)
— O3	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.65(4)
— O1	$1-x$	$-y$	$1-z$	3.85(3)
— C24	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.78(4)
— C34A	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.40(7)
— C44B	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.93(5)
C206— S3	x	y	z	3.84(3)
— C31	x	y	z	3.78(4)
— C22	x	y	z	3.86(3)
C301— S1	x	y	z	3.85(4)
C302— S3	x	y	z	3.82(5)
C303— C51	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.68(6)
— O4A	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.90(5)
— C44A	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.92(5)
C304— C51	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.68(4)
— C43	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.85(4)
C305— N2	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.99(4)
— C32	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.85(4)
— C43	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.70(5)
— C53	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.98(5)
C306— S3	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.76(4)
— C32	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.79(5)
— C13	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.95(3)
— N3	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.88(3)
— C43	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.97(4)
S1— C44A	$-x$	$-y$	$-z$	3.61(6)
S2— C52	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.97(3)
S4— C21	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.68(3)
S5— C53	$-x$	$1-y$	$-z$	3.63(2)
S6— C44A	$-x$	$-y$	$-z$	4.00(5)
— C34B	$-x$	$-y$	$-z$	3.63(6)
S7— C31	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.88(3)
— C42	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.90(3)
— C43	$-x$	$1-y$	$-z$	3.86(3)
S8— C54	$-x$	$-y$	$-z$	3.94(5)
C31— O3	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.32(4)
C41— C42	x	$-1+y$	z	3.95(4)
— O2	x	$-1+y$	z	3.61(3)
— C33	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	3.79(4)
O1— C42	x	$-1+y$	z	3.48(5)
— O2	x	$-1+y$	z	3.26(2)
— O3	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.91(3)
C22— O4A	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.41(5)
— C34A	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.72(5)
— O4B	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.46(5)
C32— O4A	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.47(5)
— O4B	$1+x$	$\frac{1}{2}-y$	$\frac{1}{2}+z$	3.25(5)
O2— C24	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.82(4)
— C44B	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	3.53(6)
C43— C24	$-x$	$1-y$	$-z$	3.73(4)
— C34A	$-x$	$1-y$	$-z$	3.99(5)
O3— C24	$-x$	$1-y$	$-z$	3.88(3)
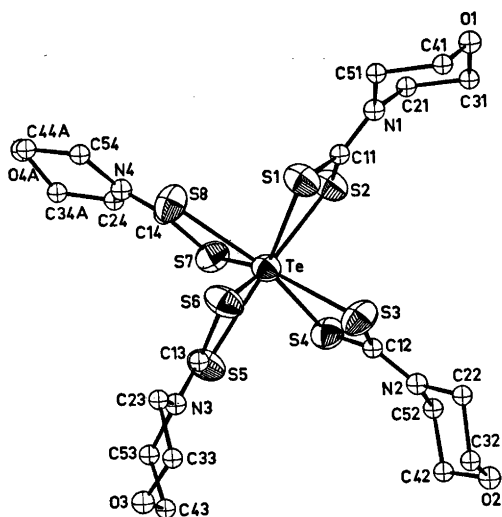
Fig. 1. The molecule as seen along the *a* axis after rotation $+12°$ around the c^* axis.

Table 8. Least squares planes through groups of atoms in the tetrakis(4-morpholinecarbo-dithioato)tellurium(IV) molecule. The first row lists atoms defining a plane, the next its equation. (Input coordinates from Table 1 gives distance from plane in Å). The next rows list atoms and their distance in Å from the plane.

Plane 1. TeS1S2S5S6

$4.696X + 6.877Y + 13.830Z - 4.311 = 0$

Te	S1	S2	S5	S6	C11	N1	C21	C51
−0.017	−0.040	0.034	−0.023	0.045	0.136	0.299	0.434	0.133

C13	N3	C23	C53
0.111	0.304	0.194	0.258

Plane 2. TeS3S4S7S8

$5.805X + 9.662Y - 18.665Z = 0$

Te	S3	S4	S7	S8	C12	N2	C22	C52
0.002	−0.032	0.050	−0.049	0.029	0.026	0.098	−0.045	0.040

C14	N4	C24	C54
−0.040	−0.115	−0.131	−0.081

Plane 3. S1S2C11N1C21C51

$5.819X + 7.680Y + 11.149Z - 4.014 = 0$

Te	S1	S2	C11	N1	C21	C51
0.179	0.042	−0.089	0.033	0.068	0.042	−0.096

Plane 4. S3S4C12N2C22C52

$6.224X + 9.539Y - 18.891Z - 0.005 = 0$

Te	S3	S4	C12	N2	C22	C52
−0.016	−0.011	−0.015	0.003	0.076	−0.031	−0.022

Plane 5. S5S6C13N3C23C53

$3.958X + 6.291Y + 15.444Z - 4.194 = 0$

Te	S4	S5	C13	N3	C23	C53
0.129	−0.056	0.015	0.013	0.104	−0.072	−0.005

Plane 6. S7S8C14N4C24C54

$5.227X + 9.703Y - 18.553Z - 0.027 = 0$

Te	S7	S8	C14	N4	C24	C54
−0.065	−0.002	0.007	0.002	−0.025	0.015	0.003

Some interplanar angles:

Angle				
1−2	90.2°	4−6	4.0
1−3	6.8	3−4	83.1
1−5	4.4	3−6	85.2
2−4	1.7	5−4	93.9
2−6	2.4	5−6	95.7
3−5	11.2		

Observed and calculated structure factors can be obtained from the author S.H. upon request.

The scattering factors were taken from the *International Tables* [22] and those for sulfur and tellurium were corrected for anomalous dispersion according to Cromer.[23] The intensity data were corrected for Lorentz and polarization effects but not for secondary extinction and absorption ($\mu=10.3$ cm^{-1}). Final atomic coordinates are listed in Table 1 and components of atomic vibration tensors in Table 2. Interatomic distances and angles are listed in Tables 4−7, while least squares planes through groups of atoms are listed in Table 8.

RESULTS AND DISCUSSION

The contents of the asymmetric unit as seen along the a axis, with atoms labelled, are shown in Fig. 1. As can be seen from the figure, all eight sulfur atoms in the tetrakis(4-morpholinecarbodithioato)tellurium(IV) molecule are bonded to the central tellurium atom.

The configuration around the central tellurium atom is slightly distorted from dodecahedral D_{2d} symmetry. This corresponds to the energetically most favourable distribution of only the eight bonding electron pairs in the valency shell of tellurium.[7,18] Thus the

Fig. 2. The average tellurium coordination within a trapezoid for $Te(Et_2NCS_2)_4$ (I), $Te(OC_4H_8NCS_2)_4$ (II), and $Te(OC_4H_8NCS_2)_2$ (III).

lone pair is again stereochemically inert in the sense that it does not occupy a position in the coordination polyhedron. A square antiprismatic configuration is also energetically favourable for eight coordination. For complexes with four bidentate ligands, the choice between the two configurations may depend on the ligand "bite" which is defined by Blight and Kepert as the distance between the donor atoms in a ligand divided by the donor atom to central atom bond length.[24] The bite in the present investigation is 1.07 ($=m$ in Table 3), making the two configurations about Te equally probable.[24]

A regular dodecahedron can be vizualized as two interleaving planar trapezoids at right angles to each other.[24] In[Te(mtc)$_4$], the two trapezoids are defined by S1, S2, S5, S6 and by S3, S4, S7, S8, respectively, and their interplanar angle is 89.8°. In [Te(dtc)$_4$] with a similar structure,[7] the angle is 88.5°, but then its structure is more distorted from D_{2d} symmetry than the structure of [Te(mtc)$_4$].

The average coordination within a trapezoid is shown in Fig. 2. The least squares planes through the TeS$_4$ groups in the two trapezoids (Table 8) show them to be nearly planar. They are also somewhat similar to the TeS$_4$ group in the corresponding divalent complex, [Te(mtc)$_2$],[21] shown in Fig. 2. In this respect, [Te(mtc)$_4$] does not differ from [Te(dtc)$_4$]. In addition, the structure of the trisulfide, [(mtc)$_2$S] is now known.[26]

Dodecahedral and square antiprismatic eight coordination have been studied in some detail by several workers.[24,25] The eight corners in a dodecahedral configuration are not equivalent, there being four corners of type A and four of type B. In [Te(mtc)$_4$] as in [Te(dtc)$_4$], the chelation is along edges m. Atoms S1, S4, S6, and S7 are located at A positions, while the other sulfur atoms are at the B positions.

Among the parameters used to describe a dodecahedron are θ_A, θ_B, MA/MB.[25] θ_A (θ_B) represents the angle between bonds MA(MB) from the central atom, M, to ligand atoms of type A(B), and the unique axis. In the present structure as well as for [Te(dtc)$_4$], the "unique axis" in the distorted dodecahedron is taken as the line joining the midpoint of the A−A(B−B) contacts in the two trapezoids with the tellurium atom. The average θ_A and θ_B angles
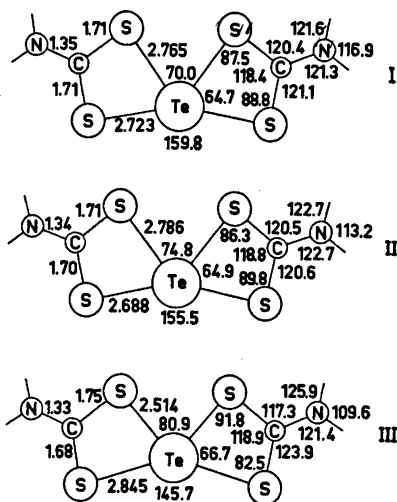
were then calculated on this basis.

In Table 3, values are given for the various dodecahedral parameters for [Te(mtc)$_4$], and for comparison, those of [Te(dtc)$_4$],[7] [Ti(dtc)$_4$][27] and [V(dta)$_4$],[28] all with approximate D_{2d} symmetry. In addition, the parameters for the energetically most "favourable" dodecahedron are included.[25]

From the table, it can be seen that the structural parameters for the four eight-coordinated dithiocarbamates are similar. Since Ti(IV) and V(IV) have smaller radii than Te(IV), the ligand bite as defined above, corresponding to m in the table, is smallest for the tellurium complexes. However, [Te(mtc)$_4$] is significantly different from the other complexes with respect to a. The parameter a is equal to the average $S_A - S_A$ distance within the two trapezoids of the dodecahedron, divided with the average $M - S$ bond length. The average $S_A - S_A$ distance in a trapezoid is 3.39 Å for [Te(mtc)$_4$] as compared to 3.17 Å for [Te(dtc)$_4$].[7] This is reflected in the larger average $S_A - Te - S_A$ angle of 74.8° in [Te(mtc)$_4$] as compared to 70.0° for the corresponding angle in [Te(dtc)$_4$]. The $S_B - Te - S_B$ angles then vary in the opposite manner due to the planarity of the trapezoids and the constancy of the intrachelate $S_A - Te - S_B$ angles.

A possible mechanism suggested for the breakdown of tetrakis(diethyldithiocarbamato)-tellurium(IV) into divalent tellurium complex and tetraethylthiuram disulfide, involved formation of disulfide by means of a $S_A - S_A$ bond being formed and the four $Te - S$ bonds within one trapezoid being broken. The other trapezoid, with some adjustment of bond lengths and angles gives the divalent tellurium complex.[7]

According to the above, the $S_A - S_A$ distance in a trapezoid should be of major importance for the stability of such eight-coordinated tellurium complexes. Thus, the greater this $S_A - S_A$ distance, the more difficult the $S_A - S_A$ bond formation, and the more stable the complex should be. The fact that the minimum $S_A - S_A$ distance in [Te(mtc)$_4$] is 0.14 Å greater than the corresponding distance in [Te(dtc)$_4$] is in accord with the greater stability of the former complex. However, the difference in the $S_A - S_A$ distances may partly be due to packing effects, and

thus may not fully account for the difference in stability found in solution.

The $Te - S_A$ and $Te - S_B$ bond lengths range from 2.74 to 2.82 and from 2.67 to 2.70 Å, respectively, and the average $Te - S$ bond length is 2.737 Å. This latter value is very close to 2.744 Å, the corresponding bond length found for [Te(dtc)$_4$].[7] Thus the dodecahedral radius of Te(IV) seems to be close to 1.70 Å. This may be compared to the octahedral radius of Te(IV) of 1.55 Å and the radius of 1.64 Å found for Te(II) in planar four-coordinated complexes.[29]

This large dodecahedral radius may in part be due to the antibonding nature of the lone pair, and to steric crowding. In favour of the latter effect is the structure of [TeI$_6$]$^{2-}$,[30] where Te(IV) has a larger radius than in the chlorine and bromine analogs.[10,31] Also attempts made at this laboratory to prepare crystals of dialkyldithiocarbamates of tetravalent selenium has so far been unsuccessful.

Recent MO calculations on IF$_7$, BrF$_5$, AsF$_5$, PF$_5$ and nuclear quadruple measurements on [TeCl$_6$]$^{2-}$ have indicated that d-orbitals only make minor contributions to the bonding in these compounds.[32-34] It is therefore possible that they also for [Te(mtc)$_4$] and related compounds make but a small contribution. Full contribution of high energy d-orbitals on tellurium to the tellurium-sulfur bonds, will, however, also have a bond lengthening effect.

The ligands are nearly planar (Table 8) and the average $C - S$ and $C - N$ bond lengths of 1.71 and 1.34 Å, respectively, are normal, both corresponding to π-bond orders near 0.3. All bond lengths in the benzene rings and in the morpholyl groups, except for the disordered one, are in the expected range.

The packing of the molecules in the unit cell is shown in Fig. 3. The benzene rings are stacked in pairs across twofold screw axes and centres of symmetry and thus form long rows parallel with the b axis. They make normal van der Waals contacts (Table 7) with each other, but there are several short contacts to the S1—S2 and S5—S6 ligands in the complex molecules. These short contacts may explain why the $S_A - S_A$ distance in the trapezoid defined by these ligands is 0.17 Å larger than the corresponding distance in the other trapezoid. There is however, no tendency
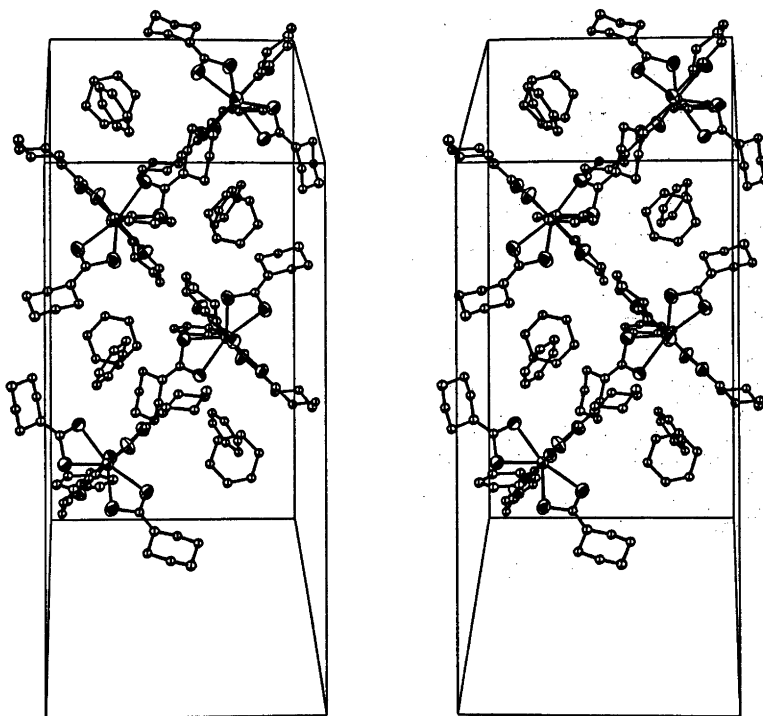
Fig. 3. A stereoscopic drawing showing the packing of molecules as seen along the *a** axis.

to adduct formation. The tetrakis(4-morpholinecarbodithioato)tellurium(IV) molecules themselves make normal van der Waals contacts with each other.

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