Studies on Tellurium–Carbon Bonded Compounds. Part 1. The Crystal Structure of 3,3-Dimethylpentane-2,4-dionato(2−)-C^1,C^5-tellurium(II)

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The structure of the title compound has been determined by the heavy-atom method from 765 reflections, measured with a diffractometer, and refined by full-matrix least-squares methods to R 0.033. Crystals are orthorhombic, space group *Pmnb*, a = 9.37(1), b = 7.96(1), c = 10.93(1) Å, Z = 4. In the discrete molecules of the complex a tellurium atom is bonded to one bivalent pentane-2,4-dione ligand *via* the two α-carbon atoms [Te-C 2.168(5) Å, C–Te–C 86.4(2)°]. This structure is the first to be reported wherein a pentane-2,4-dione ligand binds in this manner. All hydrogen atoms have been located and refined. There is no evidence for any hydrogen-bonding between the molecules.

As early as 1920, much preparative work on pentane-2,4-dionato- (acetylacetonato) complexes of many of the elements had been reported.[1] In the majority of these the pentane-2,4-dionato-ligand was univalent, bonding *via* the oxygen atoms, and many of their structures have been investigated by *X*-ray crystallography in recent

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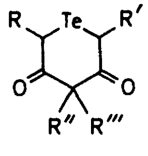
[1] G. T. Morgan and H. D. K. Drew, *J. Chem. Soc.*, 1920, **117**, 1456, and refs. therein.

years.[2-8] Only in the case of sulphur was the ligand believed to bond *via* the carbon atoms.[9]

In 1901, Werner[10] described a group of platinum compounds formed from the reaction of potassium chloroplatinate with pentane-2,4-dione. The resulting compounds exhibited novel bonding[10] and the structures of some of these and similar compounds [both platinum-(II) and -(IV)] have been shown by *X*-ray analysis to contain either tri- or uni-functional ligands.[11-15] In the trifunctional case[11,12] the β-diketone bonds *via* the oxygen atoms of the carbonyl groups to one platinum atom and through the γ-carbon to another platinum atom. In the unifunctional case[13-15] the ligand bonds to the platinum solely *via* the γ-carbon. The ligand has also been found to bond to platinum in the normal manner.[16]

Morgan and his co-workers found that on condensing certain pentane-2,4-dione derivatives with the tetrachlorides of selenium and tellurium, the pentane-2,4-dione functioned as a bivalent bidentate ligand,[17-22] the condensation taking a different course from the recorded reactions with other elements and giving compounds of type (1). We have previously[23] reported ^{13}C- and ^{1}H-n.m.r. data for 3,3-dimethylpentane-2,4-dionato(2 −)-*C*^{1},*C*^{5}-tellurium(II), and these data confirm Morgan's proposed structure.



(1)

Very few *X*-ray crystal structures of tellurium complexes are known and the only one of a tellurium(II) organometallic containing a bivalent ligand is that of phenoxatellurine.[24] We now report the structure of 3,3-dimethylpentane-2,4-dionato(2 −)-*C*^{1},*C*^{5}-tellurium(II) (1; R = R′ = H; R″ = R‴ = Me) the first to be performed on a compound wherein the β-diketone bonds through the α-carbon atoms.

EXPERIMENTAL

Air-stable golden crystals, suitable for *X*-ray analysis, were obtained from the museum in the Chemistry Department of this University and are almost certainly originals from Morgan's time.[1,17-22] Unit-cell and space-group data were obtained photographically and intensity data with a diffractometer.

Crystal Data.—$C_7H_{10}O_2Te$, $M = 253.8$, Orthorhombic, $a = 9.37(1)$, $b = 7.96(1)$, $c = 10.93(1)$ Å, $U = 815.2$ Å^3, $D_m = 2.09$ g cm^{-3}, $Z = 4$, $D_c = 2.07$ g cm^{-3}, $F(000) = 480$. Space group *Pmnb* (D_{2h}^{16}, No. 62, in a non-standard setting) or $P2_1nb$ (C_{2v}^{9}, No. 33, in a non-standard setting) from systematic absences: $h0l$ when $h + l \neq 2n$ and $hk0$ when $k \neq 2\ n$, the former being confirmed by the successful structure refinement. Mo-K_α radiation, $\lambda = 0.7107$ Å; μ(Mo-K_α) = 33.3 cm^{-1}. Single-crystal precession and Weissenberg photographs, and diffractometer data.

Structure Determination.—Intensity data were collected about the *a* axis (layers 0—9kl) with a Stoe two-circle computer-controlled diffractometer, by use of graphite monochromated Mo-K_α radiation. The stationary-counter–moving-crystal method was used, with an ω-scan range of 2.0° on the lower levels, counting for 1 s at 0.01° intervals. For reflections on the fourth and higher layers ($\mu > 7°$) a variable range was scanned, with $\Delta\omega$ defined by ($A + B \sin \mu/\tan \nu$) where $A = 1.0$ and $B = 0.5$. Stationary-background counts were measured at the extremities of each scan for 10 s. Within the range $0.1 < \sin \theta/\lambda < 0.65$, 765 independent reflections having $I > 2.5\sigma(I)$ were obtained and considered observed. Data were corrected for Lorentz and polarization factors but not for absorption since the crystal was a needle of uniform cross-section elongated parallel to the *a* axis.

The structure was solved by conventional Patterson–Fourier techniques. Scattering factors used were those for the neutral atoms,[25] with corrections for the effects of anomalous dispersion ($\Delta f'$, $\Delta f''$)[26] applied to those for tellurium. Initial refinement by full-matrix least-squares methods was with layer scale factors refined separately, and all atoms vibrating isotropically. Refinement was continued with the layer scale factors held constant and with the introduction of anisotropic thermal parameters, for all non-hydrogen atoms, of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{23}klb^*c^* + 2U_{13}hla^*c^* + 2U_{12}hka^*b^*)]$. All the hydrogen atoms of the structure were successfully located, at *ca.* 1 Å from their respective carbon atoms, and their positional parameters were refined with *U* fixed at 0.05Å^2. In the final stages of

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refinement the weighting scheme [27] $w = [\sigma^2(F_o) + (0.08|F_o|)^2]^{-1}$ was found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing sin θ/λ and with increasing fractions of $|F_o|$. At convergence no parameter shift was $>0.001\sigma$ and a final difference-Fourier map showed no significant features. The final R was 0.033 and $R' \{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ was 0.059. All calculations were carried out on the ICL 1906A at the University of Birmingham Computer Centre using SHELX-76.[28] Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21931 (8 pp.); * the final positional parameters and anisotropic temperature factors, with their estimated standard deviations, are in Table 1, and interatomic distances and angles in Table 2.

TABLE 1

Atomic positional and thermal parameters (× 10^3), with least-squares estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Te	0.75	0.504 64(5)	0.608 11(4)	34.0(5)	38.4(3)	28.7(3)	−11.4(1)	0	0
C(1)	0.591 6(5)	0.310 0(6)	0.579 5(5)	35.3(10)	40.8(20)	30.0(19)	9.1(19)	10.1(18)	0.7(17)
C(2)	0.615 2(4)	0.251 8(5)	0.449 3(4)	27.6(9)	26.5(17)	28.5(19)	−1.3(15)	4.3(14)	−1.7(12)
C(3)	0.75	0.145 8(7)	0.420 8(6)	26.3(11)	30.0(23)	22.4(23)	1.8(21)	0	0
C(4)	0.75	0.097 2(10)	0.282 7(6)	36.5(15)	46.2(32)	26.8(28)	−10.7(26)	0	0
C(5)	0.75	−0.014 8(10)	0.496 8(11)	47.6(21)	34.0(35)	61.0(49)	5.1(32)	0	0
O	0.531 1(4)	0.286 9(5)	0.369 0(3)	38.9(8)	42.0(17)	37.0(14)	−4.3(14)	−7.2(15)	6.5(15)
H(11)	0.504(7)	0.361(8)	0.586(6)	*					
H(12)	0.602(6)	0.214(8)	0.639(7)	*					
H(41)	0.658(8)	0.029(7)	0.282(7)	*					
H(42)	0.75	0.194(11)	0.187(8)	*					
H(51)	0.678(6)	−0.072(9)	0.484(6)	*					
H(52)	0.75	0.006(9)	0.579(14)	*					

* Isotropic, parameter held at 0.05Å^2.

TABLE 2

Interatomic distances (Å) and angles (°), with estimated standard deviations in parentheses

(*a*) Distances

Te–C(1)	2.168(5)	C(3)–C(5)	1.52(1)
C(1)–H(11)	0.92(6)	C(4)–H(41)	1.02(7)
C(1)–H(12)	1.01(7)	C(4)–H(42)	1.30(9)
C(1)–C(2)	1.513(7)	C(5)–H(51)	0.83(6)
C(2)–O	1.212(5)	C(5)–H(52)	0.92(15)
C(2)–C(3)	1.550(5)	Te · · · O$^{\text{I}}$	3.123(4)
C(3)–C(4)	1.559(9)		

(*b*) Angles

C(1)–Te–C(1$^{\text{II}}$)	86.4(2)	C(2)–C(3)–C(4)	109.2(3)
Te–C(1)–H(11)	107(4)	C(2)–C(3)–C(5)	110.3(4)
Te–C(1)–H(12)	113(3)	C(4)–C(3)–C(5)	108.6(6)
Te–C(1)–C(2)	104.7(3)	C(3)–C(4)–H(41)	98(4)
H(11)–C(1)–H(12)	112(5)	C(3)–C(4)–H(42)	129(4)
H(11)–C(1)–C(2)	110(4)	H(41)–C(4)–H(42)	108(5)
H(12)–C(1)–C(2)	111(4)	H(41)–C(4)–H(41$^{\text{II}}$)	115(5)
C(1)–C(2)–O	121.0(4)	C(3)–C(5)–H(51)	112(5)
C(1)–C(2)–C(3)	118.3(4)	C(3)–C(5)–H(52)	112(5)
O–C(2)–C(3)	120.7(4)	H(51)–C(5)–H(52)	106(5)
C(2)–C(3)–C(2$^{\text{II}}$)	109.1(4)	H(51)–C(5)–H(51$^{\text{II}}$)	109(7)

Roman numeral superscripts refer to atoms in the following equivalent positions:

I $1 - x, 1 - y, 1 - z$ II $\frac{3}{2} - x, y, z$

DISCUSSION

The structure consists of discrete molecules of the complex (Figures 1 and 2) which are bisected by the mirror planes at $x = 1/4$ and $3/4$. The atoms lying on the mirror planes are the tellurium atom as well as C(3), C(4), C(5), H(42), and H(52).

The β-diketone skeleton in the present complex is unique to tellurium and selenium chemistry. The tellurium atom has a formal oxidation state of +2 and the ligand is therefore bivalent. Such a structure has not, hitherto, been reported. The tellurium atom bonds to the two α-carbon atoms [C(1), C(1$^{\text{II}}$)] of the ligand at a distance of 2.168(5) Å; this distance is significantly longer than those in phenoxatellurine [24] [Te–C 2.093(9), 2.104(8) Å]. The α-carbons in turn bond to the carbonyl carbons [C(2), C(2$^{\text{II}}$); C–C 1.513(7) Å] and to two hydrogen atoms [H(11), H(12)]. The C–O carbonyl distance [1.212(5) Å] is typical of a ketonic carbonyl.[13-15,29] The γ-carbon atom C(3) is bonded to the two carbonyl carbons [C–C 1.550(5) Å] and to two methyl groups [C(4), C(5)]. The resulting six-membered heterocyclic ring, of chair conformation (Figure 2), is quite different to the planar rings found in normal pentane-2,4-dione compounds; [2-8] the six-membered ring in phenoxatellurine has the boat conformation.[24]

The stereochemistry of the tellurium atom can be described on VSEPR theory [30] as being derived from a tetrahedron, with two positions occupied by non-bonding electron pairs. The C(1)–Te–C(1$^{\text{II}}$) angle [86.4(2)°] is considerably smaller than the tetrahedral value and results from repulsion due to the presence of the two lone-pairs on the *sp*^{3}-hybridized tellurium(II) atom. The corresponding angle in phenoxatellurine [24] is 89.4(3)°.

The closest non-bonding contacts in the structure are between Te and O$^{\text{I}}$ [3.123(4) Å]; all other non-hydrogen atom intermolecular distances are >3.45 Å. There is no evidence for any hydrogen bonding between the molecules.

Figures 1 and 2 show the approximate directions of the lone-pairs on the tellurium atoms, and that they are directed into the only space in the structure. More-

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* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1976, Index issue.

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over, the lone-pairs on neighbouring tellurium atoms are aligned so that they do not directly oppose, but are parallel to one another. The packing appears to result from sideways repulsion of the lone-pairs and weak van der Waals forces between the molecules.

The golden colour of the present compound may be caused by weak associations between the tellurium atoms themselves (Te ··· Te 5.05 Å) or between the tellurium lone-pairs on neighbouring molecules used in a similar manner to that described previously.[31,32] This would be in agreement with the results of McCullough [33] who found that linear chain interactions of the type ··· I–Te–I ··· I–Te–I ··· in similar compounds were red, I ··· I interactions were violet, and that longer associations in solution were yellow. In the present compound, which is a golden colour, the associations are long (5.05 Å) and in phenoxatellurine,[24] which is pale yellow, the Te ··· Te distance (6.04 Å) is even longer. Evidence for little electron density being donated into the ' bands ' is seen by the large deviation of the C–Te–C angle from the tetrahedral value, which is caused by the presence of the lone-pairs, and also that only minimal overlap can occur between tellurium orbitals at such long distances.

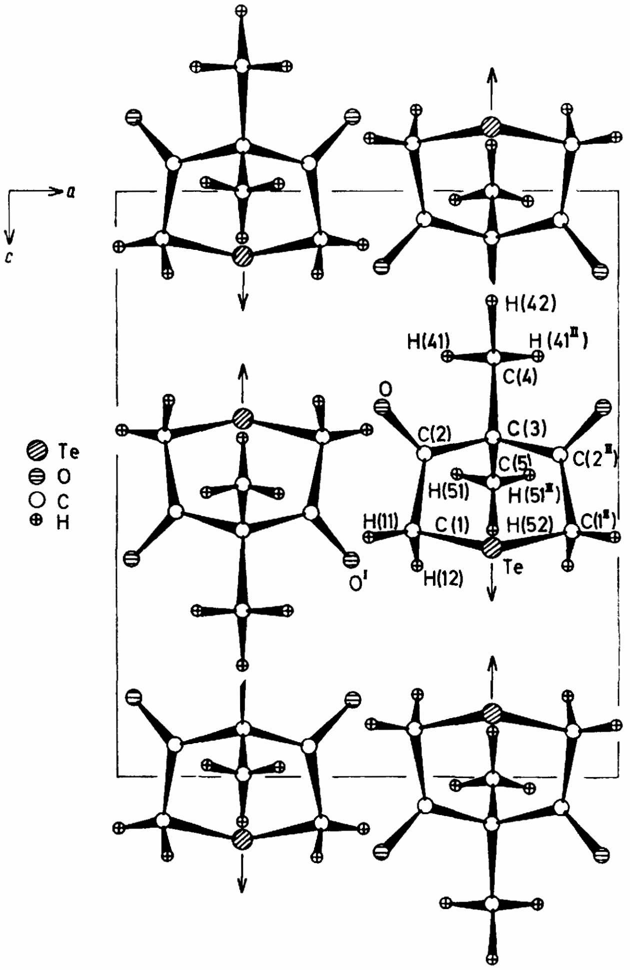

FIGURE 1 Projection of the structure down [010]. The C(4) methyl groups of two of the molecules have been omitted for clarity. Arrows indicate the approximate directions of the tellurium lone-pairs

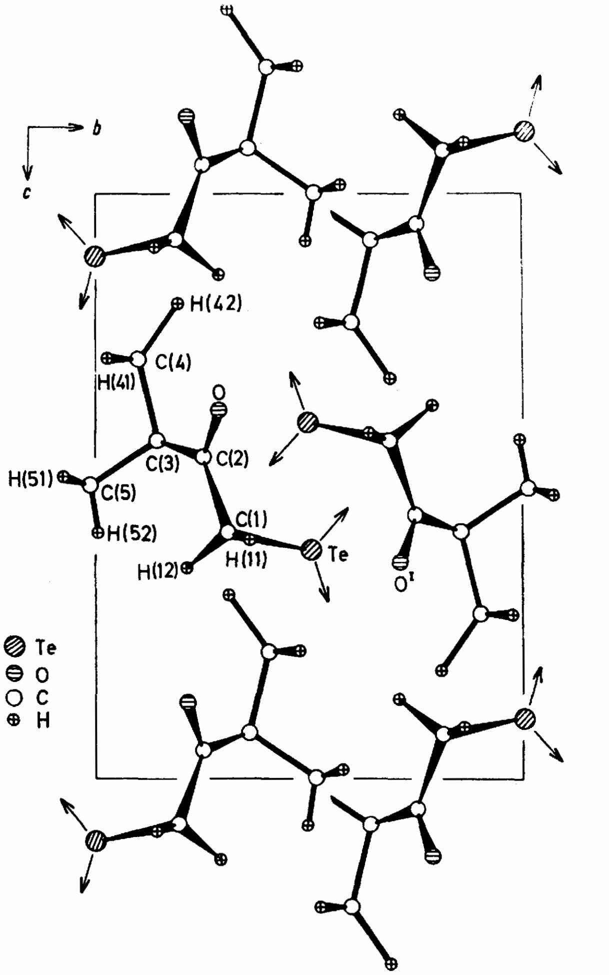

FIGURE 2 Projection of the structure down [100]. The C(5) methyl groups of two of the molecules have been omitted for clarity. Arrows indicate the approximate directions of the tellurium lone-pairs

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