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Studies on Tellurium–Carbon Bonded Compounds.
III.* The Crystal Structure of Acetylacetone Tellurium(II)

BY JOHN C. DEWAN AND JACK SILVER

*Chemistry Department, University of Birmingham, PO Box 363, Birmingham B15 2TT, England*

The structure of the title compound has been determined by the heavy-atom method from 685 reflexions, measured with a diffractometer, and refined by full-matrix least-squares methods to R 3·4%. Crystals are orthorhombic, space group $Iba2$, $a = 22·35$ (3), $b = 10·78$ (2), $c = 5·26$ (1) Å, $Z = 8$. In the molecules of the complex a Te^{II} atom is bonded to one bivalent acetylacetone ligand *via* the α-C atoms [Te–C 2·17 (1), 2·15 (1) Å; C–Te–C 90·8 (4)°] forming a heterocyclic ring of chair conformation. The molecules are arranged into one-dimensional polymers parallel to [001] by associations between the Te atoms: the implications of these associations with regard to the colour of this and related tellurium compounds are discussed in the light of present theories. H atoms could not be located.

Introduction

Many crystal structures of acetylacetone complexes have been investigated by X-ray analysis in recent years (Anderson, Neuman & Melson, 1973; Dymock & Palenik, 1974; Hon & Pfluger, 1973; Montgomery & Lingafelter, 1964; Morosin, 1965, 1967; Morosin & Montgomery, 1969) and in all of these the ligand bonds *via* the O atoms behaving as a univalent bidentate ligand. The only anomalous examples so far reported are with Pt^{II}, Pt^{IV} and S (Figgis, Lewis, Long, Mason, Nyholm, Pauling & Robertson, 1962; Hazell, Swallow & Truter, 1959; Jones & Power, 1976; Mason, Robertson & Pauling, 1969; Swallow & Truter, 1960, 1962). In these cases the ligand can be either uni- or trifunctional. In the unifunctional case the ligand bonds to the Pt or S atom solely *via* the γ-C atom, and in the trifunctional case the β-diketone bonds *via* the O atoms of the carbonyl groups to one Pt atom and through the γ-C to another Pt atom.

We have previously reported NMR data (Dewan & Silver, 1976a) and the crystal structures of 3,3-dimethylacetylacetone tellurium(II) (*A*) and 1,1'-dimethylacetylacetone tellurium(II) (*B*) (Dewan & Silver, 1976b,c) wherein the β-diketone acts as a bivalent bidentate chelate bonding to the Te^{II} atom *via* the α-C atoms. This is the first time that acetylacetone derivatives have been shown by X-ray analysis to bind in this manner. These Te compounds were prepared and reported by Morgan and co-workers (Morgan, 1925; Morgan & Drew, 1920, 1922, 1924a,b, 1925;
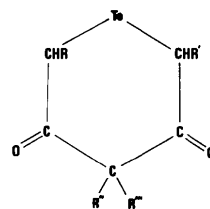
(A): R = R' = H ; R'' = R''' = CH$_3$

(B): R = R' = CH$_3$; R'' = R''' = H

(C): R = R' = H ; R'' = R''' = H

* Part II: Dewan & Silver (1976c).

Morgan & Porter, 1924) in the early 1920's. The only other crystal structure of a Te^{II} organometallic compound containing a bivalent bidentate chelate is that of phenoxatellurine (Smith, Mangion, Zingaro & Meyers, 1973).

The range of yellow seen in these compounds can be correlated with the Te—Te distances. McCullough (1973) has previously noted the significance of $I \cdots I$ and $\cdots I-Te-I \cdots I-Te-I \cdots$ links in Te^{IV} structures and how such associations are found to give rise to specific colours. Unassociated Te^{II} compounds are found to be colourless (Blackmore & Abrahams, 1955). Also, colour and electrical properties have been connected with donation of electron density into 'bands' in compounds of such p-block elements (Donaldson & Silver, 1974; Donaldson, Silver, Hadjiminolis & Ross, 1975). As a continuation of our study in this area we now report the structure of acetylacetone tellurium(II) (C).

Experimental

Crystals suitable for X-ray analysis were obtained from the museum in the Chemistry Department of this University and are almost certainly originals from the time of Morgan.

Approximate cell dimensions were determined by oscillation, Weissenberg and precession photographs, final cell dimensions being measured on a Stoe two-circle computer-controlled semi-automatic diffractometer with graphite-monochromated Mo $K\alpha$ radiation and a scintillation counter. Intensities were collected from a crystal of dimensions $0.05 \times 0.15 \times 1.15$ mm mounted about the c axis (layers $hk0$–5). The stationary-counter—moving-crystal method was used, with an ω-scan range of $2.0°$ on the lower levels, counting for 0.15 s at $0.01°$ intervals. This corresponds to a scan rate of $4°$ min^{-1}. For reflexions on the second and higher layers ($\mu > 7°$) a variable range was scanned, with $\Delta \omega$ defined by $(A + B \sin \mu/\tan \theta')°$ where $2\theta'$ is the azimuth angle (Buerger, 1942) and A and B were

assigned values of 1.0 and 0.5 respectively. Stationary-background counts were measured at the extremities of each scan for 10 s. Within the range $0.1 < \sin \theta/\lambda \le 0.65$, 685 independent reflexions having $I > 2.5\sigma(I)$ were obtained and considered observed. Data were corrected for Lorentz and polarization factors as well as for absorption.

Crystal data

$C_5H_6O_2Te$, $M_r = 225.7$, orthorhombic, $a = 22.35$ (3), $b = 10.78$ (2), $c = 5.26$ (1) Å, $U = 1267.3$ Å^3, $D_m = 2.38$, $D_c = 2.37$ g cm^{-3}, $Z = 8$, $F(000) = 832$. Space group $Iba2$ (C_{2v}^{21}, No. 45) or $Ibam$ (D_{2h}^{26}, No. 72) from systematic absences: hkl when $h + k + l \ne 2n$, $0kl$ when $k \ne 2n$, and $h0l$ when $h \ne 2n$, the former being confirmed by the successful structure solution and refinement. Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å; $\mu = 42.9$ cm^{-1}).

Structure determination

The coordinates of the Te atom were determined from a Patterson synthesis. The non-centrosymmetric space group $Iba2$ was assumed and structure factors were calculated (R 19%) followed by a Fourier synthesis based on the calculated phases. This electron density map showed the expected pseudosymmetry with one molecule and its mirror image, both sharing a common Te atom, lying on opposite sides of a pseudo mirror plane at $z = \frac{1}{2}$. This indicated that the mirror plane was not genuine and the pseudosymmetry was broken by refining the Te atom and the C atom, bonded to the Te, that had the highest peak height of the four possibilities. The remaining atoms of this molecule were easily located but refinement would not fall below an R of 10%, even with all atoms vibrating anisotropically. At this stage an absorption correction was applied and refinement, by full-matrix least-squares methods, was continued. At this point it was noted that the z coordi-

Table 1. *Fractional atomic coordinates and anisotropic thermal parameters (all* $\times 10^4$*, except* Te *positional* $\times 10^5$) *with estimated standard deviations in parentheses*

Anisotropic temperature factors are in the form: $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{23}klb^*c^* + \cdots)]$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Te	43359 (2)	36348 (5)	50000	297 (4)	320 (4)	321 (6)	21 (7)	27 (5)	−38 (2)
C(1)	4381 (4)	1679 (12)	5937 (25)	233 (42)	356 (46)	293 (23)	−14 (45)	−45 (36)	12 (37)
C(2)	3873 (5)	1416 (8)	7727 (23)	282 (41)	188 (38)	232 (20)	−6 (37)	−40 (41)	−6 (30)
C(3)	3235 (6)	1541 (10)	6645 (25)	335 (50)	344 (52)	340 (26)	174 (46)	−61 (47)	2 (43)
C(4)	3098 (4)	2873 (9)	6079 (21)	198 (36)	233 (37)	214 (18)	−4 (35)	9 (34)	−39 (34)
C(5)	3415 (5)	3443 (10)	3877 (25)	253 (43)	302 (46)	277 (22)	91 (40)	−10 (44)	−34 (40)
O(1)	3982 (4)	1152 (6)	9958 (−)†	572 (48)	368 (33)	465 (23)	−159 (60)	435 (61)	−99 (32)
O(2)	2753 (4)	3482 (8)	7401 (23)	351 (40)	549 (50)	450 (23)	−79 (42)	−129 (45)	12 (36)

† Parameter not refined.

nate of O(1), which is positioned close to one of the above-mentioned pseudo mirror planes, was oscillating between its true position and the corresponding mirror image position, with alternate cycles of least-squares refinement. This problem was overcome by fixing the z coordinate of O(1) on the correct side of the mirror plane, the optimum value for z being found from a difference-Fourier map computed towards the final stages of refinement with O(1) omitted from the calculation.

In the final stages of refinement the weighting scheme $w = [\sigma^2(F_o) + (0.05|F_o|)^2]^{-1}$ was found appropriate, giving a satisfactory analysis of the variation of $w\Delta^2$ with increasing $\sin\theta/\lambda$ and with increasing fractions of $|F_o|$. At convergence no parameter shift was greater than 0.001σ, the final R was 3.4% and R' $\{ = [\Sigma\, w(|F_o| - |F_c|)^2/\Sigma\, w|F_o|^2]^{1/2}\}$ was 5.7% for the preferred hand.* Scattering factors used were those for the neutral atoms (Cromer & Mann, 1968), with corrections for the effects of anomalous dispersion $(\Delta f', \Delta f'')$ applied to those for Te (Cromer, 1965). A final difference-Fourier map

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32288 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Interatomic distances* (Å) *and angles* (°) *with estimated standard deviations in parentheses*

(a) Intramolecular distances

Te—C(1)	2.17 (1)	C(2)—C(3)	1.54 (2)
Te—C(5)	2.15 (1)	C(3)—C(4)	1.50 (1)
C(1)—C(2)	1.50 (2)	C(4)—O(2)	1.23 (1)
C(2)—O(1)	1.23 (1)	C(4)—C(5)	1.49 (2)

(b) Angles

C(1)—Te—C(5)	90.8 (4)	C(2)—C(3)—C(4)	110.3 (9)
Te—C(1)—C(2)	106.9 (7)	C(3)—C(4)—O(2)	121.9 (10)
C(1)—C(2)—O(1)	119.4 (10)	C(3)—C(4)—C(5)	116.9 (9)
C(1)—C(2)—C(3)	116.8 (10)	C(5)—C(4)—O(2)	121.2 (10)
C(3)—C(2)—O(1)	123.7 (10)	C(4)—C(5)—Te	106.3 (7)

(c) Selected intermolecular contacts

Te···Te^i	3.95 (1)	Te···Te^{viii}	6.72 (1)
Te···Te^{ii}	3.95 (1)	Te···Te^{ix}	6.72 (1)
Te···Te^{iii}	3.97 (1)	C(1)···O(1^{vi})	3.32 (1)
Te···Te^{iv}	3.97 (1)	C(1)···O(1^x)	3.22 (1)
Te···Te^v	4.18 (1)	C(2)···O(1^x)	3.14 (1)
Te···Te^{vi}	5.26 (1)	C(3)···O(2^{xi})	3.14 (2)
Te···Te^{vii}	5.26 (1)	C(4)···O(2^{xi})	3.08 (1)

Symmetry code

(i)	$x, 1 - y, -\frac{1}{2} + z$	(vii)	$x, y, 1 + z$
(ii)	$x, 1 - y, \frac{1}{2} + z$	(viii)	$1 - x, 1 - y, -1 + z$
(iii)	$1 - x, y, -\frac{1}{2} + z$	(ix)	$1 - x, 1 - y, 1 + z$
(iv)	$1 - x, y, \frac{1}{2} + z$	(x)	$x, -y, -\frac{1}{2} + z$
(v)	$1 - x, 1 - y, z$	(xi)	$\frac{1}{2} - x, \frac{1}{2} - y, -\frac{1}{2} + z$
(vi)	$x, y, -1 + z$		

showed two residual peaks of approximately 1.3 e Å^{-3} in the vicinity of O(1), but these could not be included in the model in any way and were ignored; the small peaks present did not always yield consistent H positions and, hence, none were included in our structure determination. Most of the calculations were carried out on the ICL 1906A at the University of Birmingham Computer Centre with *SHELX*-76 (Sheldrick, 1975), and with *BONDLA* and *LSQPL* being used from X-RAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) on the CDC 7600 at the University of Manchester Regional Computer Centre. Final atomic coordinates and anisotropic temperature factors are listed in Table 1, and interatomic distances and angles in Table 2.

Discussion

The molecules of the structure (Figs. 1 and 2) are associated with one another by Te—Te contacts that form polymeric chains of Te atoms running parallel to **c** (Fig. 3) and provide each Te with close contacts to five other Te atoms at distances of 3.95 (1), 3.97 (1), 4.18 (1) Å.

The mode of attachment displayed by the β-diketone in the present structure, and in those of (A) and (B), are new and appear to be unique to Te and Se chemistry. The Te has a formal oxidation state of $+2$ and the ligand is therefore bivalent. The Te atom bonds to the two α-C atoms [C(1) and C(5)] of the ligand at distances of 2.17 (1) and 2.15 (1) Å; these distances are typical of those found for Te—C bonds in other Te^{II}, and indeed Te^{IV}, organometallic compounds. The α-carbons [C(1) and C(5)] each bond to two H atoms (not located) and to the two carbonyl C atoms [C(2) and C(4)]. The C—O carbonyl distances [1.23 (1) Å] are typical of ketonic carbonyls and are similar to those in (A) and (B). The γ-carbon C(3) is bonded to the two carbonyl C and to two H atoms (not located). [The least-squares plane through C(1), C(2), C(4) and C(5) is given in Table 3.] The resulting six-membered heterocyclic ring of chair conformation is quite different from the planar rings found in the more usual acetylacetone compounds; the six-membered ring in phenoxatellurine has the boat conformation.

The closest intermolecular contacts of the structure are given in Table 2. Those involving carbonyl C atoms [C(2)···O(1^x) 3.14, C(4)···O(2^{xi}) 3.08 Å] are nonbonding contacts while those between C(1)···O(1^{vi}), C(1)···O(1^x) and C(3)···O(2^{xi}) (3.32, 3.22, 3.14 Å) are possible hydrogen-bonding interactions; however, the H atoms could not be located.

There are two possible ways of describing the hybridization of the Te atoms: either sp^2 or sp^3 in a similar manner to that for Sn^{II} (Cotton, Donaldson, Lappert & Silver, 1976). In the former, the Te atom is considered

to have a trigonal planar arrangement, with two bonds to C and a lone pair of electrons in the equatorial plane. The two other non-bonding valence electrons will occupy the p orbital at right angles to the trigonal plane. For the sp^3 case the environment is derived from a tetrahedron with two positions occupied by non-bonding electron pairs. The C—Te—C angle in the present compound [90·8 (4)°] is considerably less than either of the ideal values of 109° 28' or 120° and can be explained on VSEPR theory as resulting from lone-pair repulsion.

If an sp^2 hybridization scheme is used then the lone pairs will be opposite each other in the xy plane between adjacent molecules. The other p orbital on each Te^{II} will lie approximately along the c axis and these are then aligned, together with empty Te $4d$ orbitals (Donaldson, Laughlin, Ross & Silver, 1973), so that a weak overall bonding orbital is then possible between them. These weak associations would then account for the bright yellow colour of the compound, and this result would be in good agreement with the work of McCullough (1973).
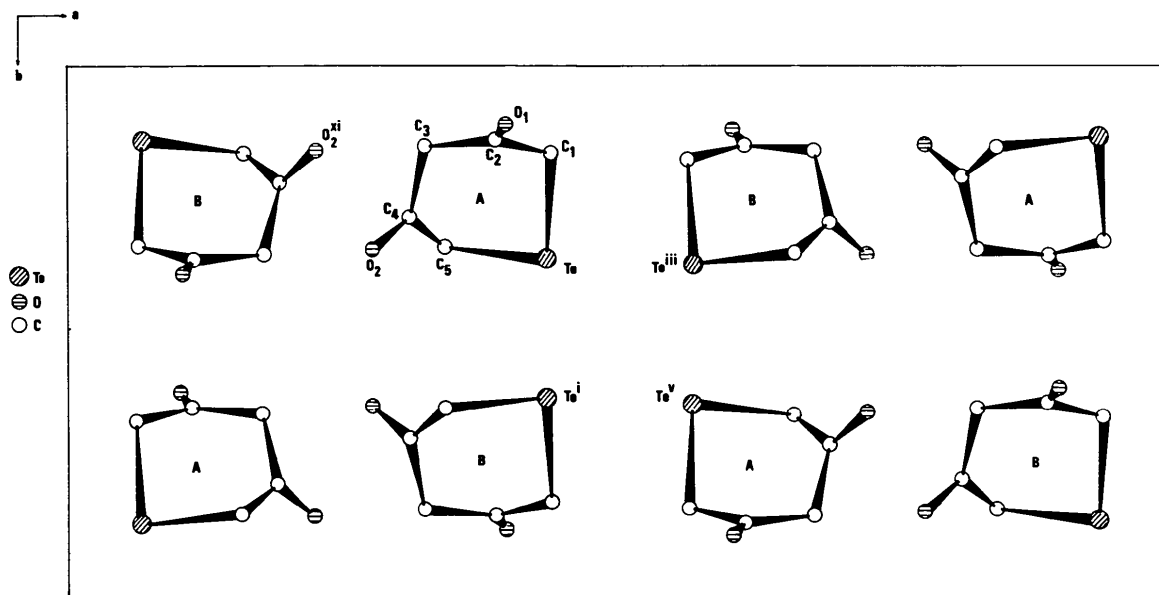

Fig. 1. Projection of the structure down [001]. Molecules marked A have Te at $z = \frac{1}{2}$, those marked B have Te at $z = 0$.
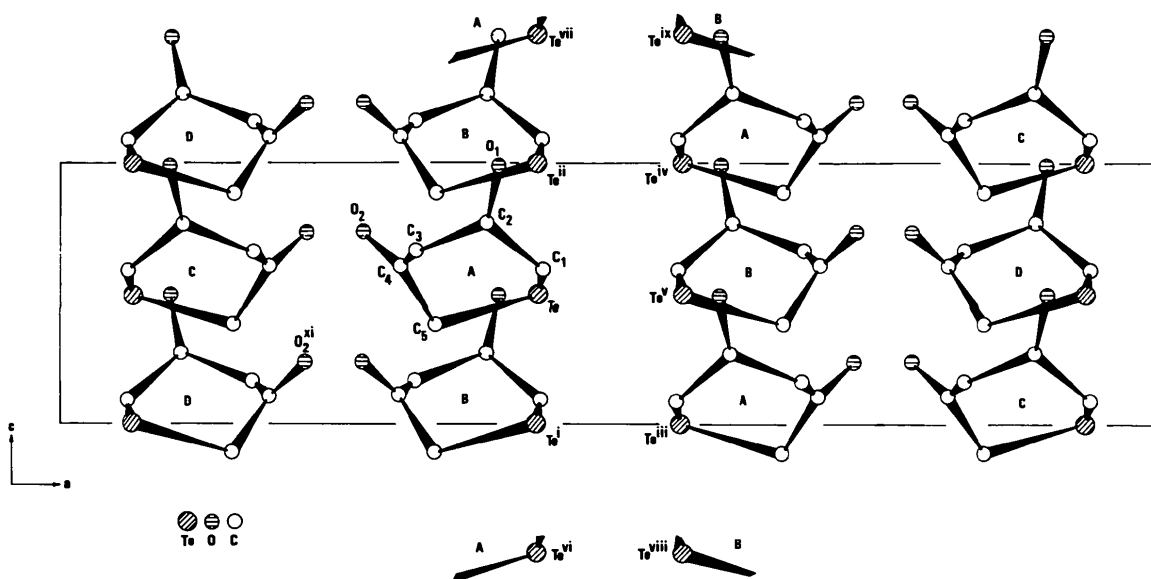

Fig. 2. Projection of the structure down [010]. Molecules marked A, B, C, and D have Te at $y = 0.36$, 0.63, 0.86, and 0.13 respectively.
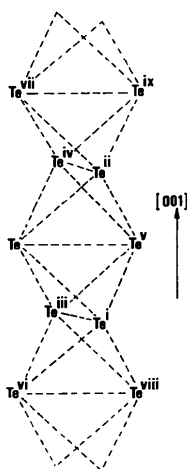
Fig. 3. Diagrammatic sketch of the Te polymer. Distances and symmetry code are given in Table 2. Te^i and Te^{ii} are in front, Te^{iii} and Te^{iv} are behind, and the remainder of the Te atoms are in the plane of the page.

In the present structure the Te$\cdots$Te distances are similar to that found in (B) (4·07 Å) and are shorter than in (A) (5·05 Å) and the colour is stronger than that of (A). Evidence for electron density in the Te$\cdots$Te associations is seen by the larger C—Te—C angle in this compound [90·8 (4)°] and in (B) [89·7 (3)°] compared with that of (A) [86·4 (2)°] which has weaker associations, showing that lone-pair repulsion is reduced, indicating less electron density remaining in the lone pairs.

Table 3. *Least-squares plane through* C(1), C(2), C(4), C(5)

The equation of the plane is $-7·57x + 7·77y + 3·18z = 6·60$, where x, y, z are the fractional coordinates of the defining atoms in the direct cell. Atomic deviations from the plane are in Å.

| Te | 1·19 | C(1) | 0·01 | C(2) | −0·01 | C(3) | −0·74 |
| C(4) | 0·01 | C(5) | −0·01 | O(1) | 0·58 | O(2) | 0·64 |

The intermolecular packing appears to be dominated by the Te$\cdots$Te associations forming one-dimensional polymers, which are joined by cross-links between the molecules from hydrogen bonds. The polymers are aligned along c and the weak Te$\cdots$Te associations in this direction seem to be responsible for this being the major direction of growth in the crystals. This is similar to results found in (B) where another type of Te polymer was found and this again was aligned in the major growth direction.

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