# Structure of Dichloro[(4,4-dimethyl-5-oxo-2,3,4,5-tetrahydro-2-furyl)methyl]-(4-methoxyphenyl)tellurium(IV) 

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#### Abstract

TeCl}_{2}\left(\mathrm{C}_{7} \mathrm{H}_{7} \mathrm{O}\right)\left(\mathrm{C}_{7} \mathrm{H}_{11} \mathrm{O}_{2}\right)\right], \quad M_{r}=432 \cdot 8\), monoclinic, $P 2_{1} / m, a=11.077$ (4), $b=9.472$ (2), $c$ $=16.222(4) \AA, \beta=101.70(3)^{\circ}, V=1667$ (2) $\AA^{3}, Z$ $=4, D_{x}=1.73 \mathrm{Mg} \mathrm{m}^{-3}, \lambda(\mathrm{Mo} K \alpha)=0.71073 \AA, \mu=$ $2.17 \mathrm{~mm}^{-1}, F(000)=848, T=296 \mathrm{~K}, R=0.036$ for 1627 observed reflections. The Te atom is in a pseudo trigonal-bipyramidal configuration with the lone pair at one of the equatorial positions. The lactone moiety is almost planar and the furan ring has the typical envelope conformation. Distances and angles are: $\mathrm{Te}-\mathrm{Cl}=2.490$ (2), 2.507 (3) $\AA ; \mathrm{Te}-\mathrm{C}=2.094$ (7), $2 \cdot 119$ (8) $\AA ; \quad \mathrm{Cl}-\mathrm{Te}-\mathrm{Cl}=174.97$ (8) ${ }^{\circ} ; \quad \mathrm{Cl}-\mathrm{Te}-\mathrm{C}=$ 89.3 (2), 88.5 (2), 88.9 (2), 87.1 (2) ${ }^{\circ} ; \mathrm{C}-\mathrm{Te}-\mathrm{C}=$ 98.3 (3) ${ }^{\circ}$.


Introduction. The development of methods of organic synthesis based on tellurium reagents has received much attention in the last few years. Because it is of interest in this field of organic chemistry, a new cyclofunctionalization reaction was developed using tellurium methodology (Comassetto \& Petragnani, 1983) and a series of $p$-methoxyphenyltellurium dichloride lactones were prepared and characterized by ${ }^{1} \mathrm{H}$ NMR and IR spectra and elemental analysis. The title compound was crystallized and its crystal structure determination was undertaken in order to confirm the reaction product.

Experimental. Crystals from chloroform at 277 K , $0.20 \times 0.22 \times 0.33 \mathrm{~mm}$; Nonius CAD-4 diffractometer; graphite-monochromated Mo $K \alpha$; cell parameters by least squares on setting angles of 21 reflections, $16^{\circ}<2 \theta<38^{\circ}$; $\omega-2 \theta$ scans, scan width $(0.80+0.35 \tan \theta)^{\circ}$, max. scan speed $6.7^{\circ} \min ^{-1}$;

[^0]range of $h k l:-12<h<12, k<10, l<17, \quad \theta_{\max }$ $=23^{\circ}$; standards $2, \overline{1}, \overline{10}, 622$ varied $\pm 2 \%$ of mean intensities over data collection; 2400 reflections measured, 2310 unique, $R_{\text {int }}=0.024,1627$ observed above $2 \sigma(I)$; Lp corrections. Structure solved by direct methods. In final cycles of least-squares refinement all non-hydrogen atoms anisotropic. H atoms included at constrained positions $[\mathrm{C}-\mathrm{H}=1.01$ (1) $\AA$ A $]$ based on those found in difference synthesis, all with fixed isotropic $U=0.06 \AA^{2}$; methyl groups refined as rigid groups. Function minimized $\sum w\left(\left|F_{o}\right|-\left|F_{c}\right|\right)^{2}$ with $w=\left[\sigma^{2}\left(F_{o}\right)+0.0042 F_{o}^{2}\right]^{-1}, 218$ parameters refined; excluding unobserved reflections $R=0.036, w R=$ 0.040 ; inspection of $F_{c}$ and $F_{o}$ values indicated a correction for secondary extinction required; $\dagger$ max. $\Delta / \sigma=0.005, \Delta \rho$ excursions within -0.54 and $0.34 \mathrm{e} \AA^{-3}$; scattering factors for non-H atoms from Cromer \& Mann (1968) with corrections for anomalous dispersion from Cromer \& Liberman (1970), for H from Stewart, Davidson \& Simpson (1965). Programs used: MULTAN80 (Main, Fiske, Hull, Lessinger, Germain, Declercq \& Woolfson, 1980), SHELX76 (Sheldrick, 1976) and ORTEP (Johnson, 1965).

Discussion. Fractional atomic coordinates and $B_{\text {eq }}$ values are listed in Table $1 . \ddagger$ The atom numbering and a view of the molecule are given in Fig. 1. Bond lengths and angles are given in Table 2. The main result of this

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communication is the confirmation of the molecular formula previously proposed. The phenyl ring is planar, to within experimental accuracy $\left[\sigma_{a v}\right.$, defined as $\left(\sum_{i} d_{i}^{2} / N-3\right)^{1 / 2}, \quad$ is $\left.0.01 \AA\right]$. As observed in other compounds (Harlow \& Simonsen, 1976; Bocelli \& GrenierLoustalot, 1981), the lactone moiety is nearly planar $\mid \sigma_{\mathrm{av}}$ on $\mathrm{C}(8), \mathrm{O}(2), \mathrm{C}(11), \mathrm{O}(3), \mathrm{C}(10)$ is $0.04 \AA \mid$ while the ring shows a typical furan-envelope conformation with $\mathrm{C}(9) 0.38$ (1) $\AA$ out of the mean plane. The $\mathrm{C}=\mathrm{O}$ bond $[C(11)-O(3)=1 \cdot 20(1) \AA]$ is in good agreement with the accepted value [1-215 (5) $\AA$; Sutton, 1965]. The two $\mathrm{C}-\mathrm{O}$ bonds are different [1.34(1), 1.45 (1) $A$; ; this is often observed in lactone derivatives and may be interpreted as due to the valence-bond resonance form $-\mathrm{C}-\stackrel{+}{\mathrm{O}}-\underset{\mathrm{O}}{\mathrm{C}}-\mathrm{C}$ (Jeffrey, Rosenstein \& Vlasse, 1967). The largest internal angles of the lactone ring are at the carbonyl carbon $\left[110 \cdot 6(7)^{\circ}\right]$ and at the oxygen [111.0(6) ${ }^{\circ}$.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters ( $\AA^{2}$ ) with e.s.d.'s in parentheses

|  | $x$ |  |  |  |  | $z$ | $B_{\mathrm{eq}}{ }^{*}$ |
| :--- | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Te | $0.7029(1)$ | $0.2580(1)$ | $1.0724(1)$ | $3.41(2)$ |  |  |  |
| $\mathrm{Cl}(1)$ | $0.5550(2)$ | $0.1729(2)$ | $0.9456(1)$ | $4.95(7)$ |  |  |  |
| $\mathrm{Cl}(2)$ | $0.8453(2)$ | $0.3264(3)$ | $1.2071(2)$ | $5.45(8)$ |  |  |  |
| $\mathrm{O}(1)$ | $0.2658(5)$ | $0.4744(6)$ | $1.2249(4)$ | $4.9(2)$ |  |  |  |
| $\mathrm{O}(2)$ | $0.8392(5)$ | $-0.0131(6)$ | $1.0177(3)$ | $4.4(2)$ |  |  |  |
| $\mathrm{O}(3)$ | $0.9060(6)$ | $-0.1400(7)$ | $0.9215(4)$ | $5.4(2)$ |  |  |  |
| $\mathrm{C}(1)$ | $0.5537(7)$ | $0.3218(8)$ | $1.1247(5)$ | $3.3(2)$ |  |  |  |
| $\mathrm{C}(2)$ | $0.5457(7)$ | $0.4619(8)$ | $1.1460(6)$ | $4.2(3)$ |  |  |  |
| $\mathrm{C}(3)$ | $0.4481(8)$ | $0.5104(8)$ | $1.1780(6)$ | $4.7(3)$ |  |  |  |
| $\mathrm{C}(4)$ | $0.3587(7)$ | $0.4166(9)$ | $1.1915(5)$ | $3.8(3)$ |  |  |  |
| $\mathrm{C}(5)$ | $0.3652(7)$ | $0.2764(9)$ | $1.1715(5)$ | $3.9(3)$ |  |  |  |
| $\mathrm{C}(6)$ | $0.4634(8)$ | $0.2295(8)$ | $1.1373(6)$ | $4.3(3)$ |  |  |  |
| $\mathrm{C}(7)$ | $0.1723(8)$ | $0.385(1)$ | $1.2435(6)$ | $5.1(3)$ |  |  |  |
| $\mathrm{C}(8)$ | $0.8328(8)$ | $-0.0237(9)$ | $1.1056(6)$ | $4.6(3)$ |  |  |  |
| $\mathrm{C}(9)$ | $0.8375(9)$ | $-0.1798(9)$ | $1.1219(6)$ | $4.9(3)$ |  |  |  |
| $\mathrm{C}(10)$ | $0.9078(7)$ | $-0.2415(8)$ | $1.0603(5)$ | $3.6(2)$ |  |  |  |
| $\mathrm{C}(11)$ | $0.8865(7)$ | $-0.1311(9)$ | $0.9913(5)$ | $3.9(3)$ |  |  |  |
| $\mathrm{C}(12)$ | $0.7179(8)$ | $0.0475(8)$ | $1.1176(6)$ | $4.3(3)$ |  |  |  |
| $\mathrm{C}(13)$ | $1.0445(9)$ | $-0.250(1)$ | $1.0933(6)$ | $5.9(4)$ |  |  |  |
| $\mathrm{C}(14)$ | $0.857(1)$ | $-0.3848(9)$ | $1.0248(7)$ | $6.1(4)$ |  |  |  |

${ }^{*} B_{\text {eq }}=\frac{4}{3} \beth_{i j} T_{i j} B_{i j}$ (Hamilton, 1959).


Fig. 1. A view of the molecule with the crystallographic numbering scheme (thermal ellipsoids are drawn at the $50 \%$ probability level).

Table 2. Interatomic distances $(\AA)$ and bond angles $\left({ }^{\circ}\right)$

| $\mathrm{Te}-\mathrm{Cl}(1)$ | 2.490 (2) | $\mathrm{Cl}(1)-\mathrm{Te}-\mathrm{Cl}(2)$ | 174.97 (8) |
| :---: | :---: | :---: | :---: |
| $\mathrm{Te}-\mathrm{Cl}(2)$ | 2.507 (3) | $\mathrm{Cl}(1)-\mathrm{Te}-\mathrm{C}(1)$ | 89.3 (2) |
| $\mathrm{Te}-\mathrm{C}(1)$ | 2.094 (7) | $\mathrm{Cl}(1)-\mathrm{Te}-\mathrm{C}(12)$ | 88.5 (2) |
| $\mathrm{Te}-\mathrm{C}(12)$ | 2.119 (8) | $\mathrm{Cl}(2)-\mathrm{Te}-\mathrm{C}(1)$ | 88.9 (2) |
|  |  | $\mathrm{Cl}(2)-\mathrm{Te}-\mathrm{C}(12)$ | 87.1 (2) |
|  |  | $\mathrm{C}(1)-\mathrm{Te}-\mathrm{C}(12)$ | 98.3 (3) |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.38 (1) | $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(6)$ | 119.3 (7) |
| $\mathrm{C}(1)-\mathrm{C}(6)$ | 1.37 (1) | $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | $120 \cdot 9$ (8) |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | 1.37 (1) | $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | 119.4 (8) |
| $\mathrm{C}(3)-\mathrm{C}(4)$ | 1.38 (1) | C(3)-C(4)-C(5) | 120.8 (8) |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.37 (1) | $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)$ | 119.1 (8) |
| $\mathrm{C}(5)-\mathrm{C}(6)$ | 1.39 (1) | $\mathrm{C}(1)-\mathrm{C}(6)-\mathrm{C}(5)$ | 120.5 (8) |
| $\mathrm{C}(4)-\mathrm{O}(1)$ | 1.37 (1) | C(3)-C(4)-O(1) | $115 \cdot 2$ (7) |
| $\mathrm{C}(7)-\mathrm{O}(1)$ | 1.42 (1) | $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{O}(1)$ | 124.0 (7) |
|  |  | $\mathrm{C}(4)-\mathrm{O}(1)-\mathrm{C}(7)$ | 119.0 (6) |
| $\mathrm{C}(8)-\mathrm{C}(9)$ | 1.50 (1) | $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{O}(2)$ | 103.6 (7) |
| $\mathrm{C}(8)-\mathrm{O}(2)$ | 1.45 (1) | $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{C}(12)$ | 115.1 (8) |
| $\mathrm{C}(8)-\mathrm{C}(12)$ | 1.49 (1) | $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{C}(12)$ | 108.2 (7) |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | 1.50 (1) | $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | 105.7 (7) |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | 1.51 (1) | $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | 101.5 (7) |
| C(10)-C(13) | 1.50 (1) | $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(13)$ | 113.8 (7) |
| $\mathrm{C}(10)-\mathrm{C}(14)$ | 1.54 (1) | $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(14)$ | 113.1 (7) |
| $\mathrm{C}(11)-\mathrm{O}(2)$ | 1.34 (1) | $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{C}(13)$ | 107.2 (7) |
| $\mathrm{C}(11)-\mathrm{O}(3)$ | 1.20(1) | $\mathrm{C}(11)-\mathrm{C}(10)-\mathrm{C}(14)$ | 110.0 (7) |
|  |  | $\mathrm{C}(13)-\mathrm{C}(10)-\mathrm{C}(14)$ | $110 \cdot 6$ (7) |
|  |  | $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{O}(2)$ | $110 \cdot 6$ (7) |
|  |  | $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{O}(3)$ | 128.2 (8) |
|  |  | $\mathrm{O}(2)-\mathrm{C}(11)-\mathrm{O}(3)$ | 121.2 (8) |
|  |  | $\mathrm{C}(8)-\mathrm{O}(2)-\mathrm{C}(11)$ | 111.0 (6) |

The coordination around $\mathrm{Te}^{\mathrm{IV}}$ may be interpreted by postulating the presence of a stereoactive lone pair on the Te atom giving rise to a pseudo trigonal-bipyramidal configuration. As has been pointed out (Cotton \& Wilkinson, 1972), the siting of this lone pair is hard to predict. In the present case it turns out to be in the equatorial plane together with $C(1)$ and $C(12)$ while the chlorines occupy the axial positions. The angle between the normal to the equatorial plane and the line through the Cl atoms is $180^{\circ}$ and $\mathrm{Cl}-\mathrm{Te}-\mathrm{Cl}$ is $174.97(8)^{\circ}$. The $\mathrm{Te}-\mathrm{C}$ bond lengths are, as in other $R_{2} \mathrm{TeCl}_{2}$ molecules (Chadha, Drake \& Kahn, 1983; Chadha, Drake \& Hencher, 1983; Ziolo \& Troup, 1983), close to that predicted from the sum of the single-bond covalent radii. The $\mathrm{C}-\mathrm{Te}-\mathrm{C}$ angle is also within the range found for these species. This angle is less than the ideal of $120^{\circ}$ and the distortion has been explained on the basis of lone-pair-bond-pair repulsions being greater than bond-pair-bond-pair repulsions (Chadha, Drake \& Khan, 1983). The shortest non-bonded $\mathrm{Te} \cdots \mathrm{Cl}$ distance $[4.956$ (2) $\AA$ ] is greater than the sum of van der Waals radii ( $4.0 \AA$ ). The ratio $\mathrm{Te} \cdots \mathrm{Cl} /$ $\mathrm{Te}-\mathrm{Cl}$ is 2.0 and so it must be presumed that the secondary $\mathrm{Te} \cdots \mathrm{Cl}$ interactions are insignificant in this compound. The intramolecular $\mathrm{Te} \cdots \mathrm{O}(2)$ distance $|3 \cdot 194(5) \AA|$ is shorter than the sum of van der Waals radii ( $3 \cdot 60 \AA$ ).

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# Structure of $\mu$-Aqua-bis( $\mu$-trifluoroacetato-O, $\mathbf{O}^{\prime}$ ) bis[bis(dimethylphenylphosphine)(trifluoroacetato)ruthenium(II)] 

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#### Abstract

C}_{40} \mathrm{H}_{46} \mathrm{~F}_{12} \mathrm{O}_{8} \mathrm{P}_{4} \mathrm{Ru}_{2}, M_{r}=1224.81\), monoclinic, $\quad P 2_{1} / c, \quad a=18 \cdot 198$ (8), $\quad b=16 \cdot 658$ (7), $\quad c=$ 18.440 (8) $\AA, \beta=115.52$ (2) ${ }^{\circ}, U=5044.6 \AA^{3}, Z=4$, $D_{x}=1.61 \mathrm{Mg} \mathrm{m}^{-3}, \quad$ Mo $K a, \quad \lambda=0.71069 \AA, \quad \mu=$ $0.724 \mathrm{~mm}^{-1}, \quad F(000)=2456, T=293 \mathrm{~K}$, final $R=$ 0.0643 for 4625 reflections with $F_{o} \geq 4 \sigma\left(F_{o}\right)$. The complex is dinuclear with the two ruthenium atoms bridged by two trifluoroacetato ligands and an aqua ligand. The $\mathrm{Ru} \cdots \mathrm{Ru}$ internuclear distance is 3.881 (1) $\AA$. The octahedral coordination of each ruthenium atom is completed by two $\mathrm{PMe}_{2} \mathrm{Ph}$ ligands and a unidentate trifluoroacetato ligand. The oxygen atoms of the unidentate trifluoroacetato ligands are hydrogen bonded to the bridging aqua ligand.


Introduction. Carboxylate anions are versatile ligands that have found wide application in transition-metal chemistry. They are found in both low- and high-oxidation-state environments, in organometallic and bioinorganic systems, and are found bonding in a surprising number of different modes to almost every metal in the transition series (Mehrotra \& Bohra, 1983). The reactivity of metal carboxylates is to be attributed to the availability of different yet energetically closely related bonding modes, and to the intermediate nature

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of the electronic properties of the ligand. It is thus not surprising to find that carboxylate complexes of the transition metals have been extensively investigated from the point of view of both their structural chemistry and their reactivity and catalytic properties (Mehrotra \& Bohra, 1983).
As part of a programme concerned with the synthesis, reactivity and catalytic properties of carboxylate complexes of ruthenium, we recently reported synthetic routes to a series of highly reactive dinuclear ruthenium(II) complexes containing bridging and monodentate carboxylato ligands (Albers, Liles, Singleton \& Jates, 1984). We now report the structure of one of these: (I).

(I) $L=\mathrm{PMe}_{2} \mathrm{Ph}$, (II) $L=(1,5$-cyclooctadiene $) / 2$
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[^1]:    $\dagger F_{\text {corr }}=F_{c} /\left[1 \cdot 0-10^{-4} \chi F_{c}^{2} / \sin \theta\right]$, where $\chi$ refined to 0.0029 in the final run.
    $\ddagger$ Lists of structure factors, anisotropic thermal parameters and H -atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42488 ( 11 pp .). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CHI 2HU, England.

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