Table 4. *Selected interatomic distances* (Å) *and angles* (°) *in the hydrogen malonate ion*

Distances	
C(1)–C(2)	1·503 (1)
C(2)–C(3)	1·523 (1)
C(1)–O(1)	1·220 (1)
C(1)–O(2)	1·303 (1)
C(3)–O(3)	1·242 (1)
C(3)–O(4)	1·257 (1)
C(2)–H(1)	0·980 (1)
C(2)–H(2)	0·992 (1)
O(2)–H(3)	0·870 (1)

Bond angles	
C(1)–C(2)–C(3)	119·8 (1)
O(1)–C(1)–C(2)	126·1 (1)
O(2)–C(1)–C(2)	112·1 (1)
O(1)–C(1)–O(2)	121·9 (1)
O(3)–C(3)–C(2)	122·0 (1)
O(4)–C(3)–C(2)	114·5 (1)
O(3)–C(3)–O(4)	123·6 (1)
C(1)–C(2)–H(1)	113·2 (2)
C(3)–C(2)–H(2)	105·1 (1)
H(1)–C(2)–H(2)	97·7 (1)
C(3)–C(2)–H(1)	107·0 (1)
C(1)–C(2)–H(2)	111·7 (1)
C(1)–O(2)–H(3)	107·3 (1)

Torsion angles	
O(1)–C(1)–C(2)–C(3)	−4·9 (1)
O(2)–C(1)–C(2)–C(3)	175·5 (1)
O(3)–C(3)–C(2)–C(1)	1·3 (2)
O(4)–C(3)–C(2)–C(1)	−178·1 (1)

mated to be 1·25 and 1·70 in the carboxylic group and 1·40 and 1·60 in the carboxylate. This is in contrast to the situation found in potassium hydrogen malonate, where the two halves of the hydrogen malonate ion are related to each other through a twofold axis (Sime, Speakman & Parthasarathy, 1970).

The two water H atoms and the carboxylic H atom are within hydrogen-bonding distance of the O atoms (H···O 2·2 Å). The geometry of the hydrogen bonds and the water molecule are given in Table 5. The short hydrogen bond $O(4^{iv})\cdots O(2)$ linking the hydrogen malonate ions end-to-end is most probably asymmetric.

Table 5. *The geometry of the water molecule and the hydrogen bonds.*

Distances are in Å and angles in degrees. The superscripts indicate atoms related to *x,y,z* in Table 2: (ii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$; (iii) $1-x, -y, 1-z$; (iv) $1+x, \frac{1}{2}-y, -\frac{1}{2}+z$.

O(5)–H(4)	0·814 (2)	$O(4^{ii})\cdots O(5)$	2·749 (1)
O(5)–H(5)	0·792 (1)	$O(4^{ii})\cdots H(5)$	1·958 (1)
H(4)–O(5)–H(5)	110·1 (3)	$O(4^{ii})\cdots H(5)–O(5)$	175·5 (2)
$O(3^{iii})\cdots O(5)$	2·789 (2)	$O(4^{iv})\cdots O(2)$	2·589 (1)
$O(3^{iii})\cdots H(4)$	1·975 (2)	$O(4^{iv})\cdots H(3)$	1·721 (2)
$O(3^{iii})\cdots H(4)–O(5)$	177·3 (1)	$O(4^{iv})\cdots H(3)–O(2)$	173·8 (1)

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New Form of *trans*-Chlorobis(2,4-pentanedionato)(triphenylphosphine)technetium(III)

By Giuliano Bandoli, Dore A. Clemente, Ulderico Mazzi and Edoardo Roncari

Laboratorio di Chimica e Tecnologia dei Radioelementi del CNR, Corso Stati Uniti, 35100 *Padova, Italy*

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Abstract. $C_{28}H_{29}ClO_4PTc$, $M_r = 595$, triclinic, $P\bar{1}$, $a = 15{\cdot}330\,(8)$, $b = 10{\cdot}369\,(5)$, $c = 9{\cdot}309\,(6)$ Å, $\alpha = 106{\cdot}82\,(11)$, $\beta = 104{\cdot}58\,(8)$, $\gamma = 92{\cdot}13\,(7)°$, $U = 1361$ Å^3, $D_c = 1{\cdot}45$ g cm^{-3}, $Z = 2$, $\mu = 7{\cdot}1$ cm^{-1}. The title complex was synthesized by treating *trans*-[Tc(PPh$_3$)$_2$Cl$_4$] with anhydrous 2,4-pentanedione. The X-ray diffraction study of this new crystalline form, designated β, confirms the molecular structural details for the α modification [Bandoli, Clemente & Mazzi (1977). *J. Chem. Soc. A*, pp. 1837–1844].

Introduction. *trans*-Tetrachlorobis(triphenylphosphine)technetium(IV) (1 g) was heated under reflux in anhydrous 2,4-pentanedione (30 ml) for 12 h, under nitrogen. The orange-red solution was evaporated to dryness *in vacuo* and the residue was treated with acetone (0·5 ml) and filtered. The yellow powder was washed with ethanol (1 ml) and then with diethyl ether (2 ml). Yellow-orange crystals were obtained from an acetone/diethyl ether mixture (yield *ca* 50%), where this second crystalline phase seems to be the most stable, for all efforts to grow crystals of the original modification (Bandoli, Clemente & Mazzi, 1977), designated α, were unsuccessful. A poorly formed crystal (0·07 × 0·13 × 0·33 mm) was used for data collection on an automatic Philips four-circle

Table 1. *Final positional* (× 10⁴) (*with e.s.d.'s in parentheses*) *and thermal* (Å² × 10²) *parameters*

The anisotropic thermal parameters are of the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2}+\ldots+2B_{12}hka^*b^*+\ldots)]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Tc	2226 (0)	212 (1)	−1149 (1)	222	222	223	59	63	85
Cl	1688 (2)	−1976 (2)	−3106 (3)	437	264	344	51	32	13
P	2769 (1)	2474 (2)	676 (2)	261	246	253	53	80	75

	x	y	z	B		x	y	z	B
O(1)	1392 (4)	−260 (5)	43 (6)	306	C(13)	2252 (7)	5041 (10)	−1956 (12)	504
O(2)	3186 (3)	−645 (5)	47 (6)	288	C(14)	3047 (7)	5250 (11)	−2331 (12)	506
O(3)	3064 (3)	530 (5)	−2394 (6)	291	C(15)	3811 (7)	4662 (10)	−1761 (12)	495
O(4)	1272 (4)	1049 (5)	−2398 (6)	309	C(16)	3762 (6)	3842 (9)	−796 (10)	375
C(1)	732 (7)	−1223 (11)	1587 (12)	518	C(17)	2100 (5)	3412 (8)	1871 (9)	287
C(2)	1523 (6)	−994 (9)	957 (10)	358	C(18)	1286 (6)	2759 (9)	1858 (10)	358
C(3)	2333 (6)	−1535 (9)	1414 (11)	400	C(19)	712 (7)	3517 (10)	2686 (11)	459
C(4)	3103 (5)	−1337 (8)	954 (9)	315	C(20)	993 (7)	4890 (11)	3536 (12)	503
C(5)	3960 (7)	−1949 (11)	1563 (12)	496	C(21)	1802 (7)	5530 (10)	3535 (12)	477
C(6)	3596 (6)	829 (10)	−4466 (11)	422	C(22)	2358 (6)	4791 (9)	2679 (11)	400
C(7)	2853 (5)	842 (8)	−3663 (9)	296	C(23)	3912 (5)	2540 (7)	2009 (9)	272
C(8)	2014 (6)	1224 (9)	−4308 (10)	353	C(24)	4557 (6)	1834 (8)	1361 (10)	343
C(9)	1294 (6)	1339 (9)	−3639 (10)	346	C(25)	5429 (6)	1858 (9)	2321 (10)	395
C(10)	445 (7)	1884 (11)	−4369 (12)	512	C(26)	5653 (6)	2555 (9)	3927 (11)	420
C(11)	2951 (5)	3619 (8)	−446 (9)	296	C(27)	4999 (6)	3214 (9)	4570 (11)	426
C(12)	2191 (6)	4224 (9)	−1013 (10)	392	C(28)	4127 (6)	3221 (8)	3635 (10)	353

diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ = 0·7107 Å) and a θ–2θ scan ($\theta_{\max}$ = 25°). The intensities of 4778 crystallographically independent reflexions were measured, of which 3120 were above the significance level of 3·0σ and these were used in the structure solution. No absorption corrections were made because of the relatively low absorption coefficient value (7·1 cm^{-1} for Mo $K\alpha$) and because no significant intensity variation for a given reflexion was observed for rotation around the ψ angle. Refinement [heavy atoms anisotropically; quantity minimized $\sum w(|F_o| - |F_c|)^2$; unit weight to each reflexion] converged at R = 0·053.* An analysis of the final distribution of $w(\Delta F)^2$ did not suggest any appropriate weighting scheme. Atomic scattering factors, including f' for Tc, Cl and P, were taken from Cromer & Waber (1965) and Cromer (1965). A list of positional and thermal parameters is given in Table 1.

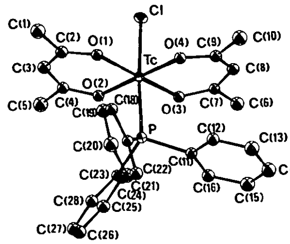

Fig. 1. The molecular structure and atomic numbering scheme. The label for C(17) is omitted for clarity.

Table 2. *Bond lengths* (Å)

E.s.d.'s average 0·01 Å.

Tc—Cl	2·42	C(4)—O(2)	1·28
Tc—P	2·44	O(3)—C(7)	1·28
Tc—O(1)	2·02	C(6)—C(7)	1·51
Tc—O(2)	2·01	C(7)—C(8)	1·40
Tc—O(3)	2·01	C(8)—C(9)	1·39
Tc—O(4)	2·02	C(9)—C(10)	1·52
O(1)—C(2)	1·28	C(9)—O(4)	1·28
C(1)—C(2)	1·51	P—C(11)	1·84
C(2)—C(3)	1·40	P—C(17)	1·84
C(3)—C(4)	1·38	P—C(23)	1·83
C(4)—C(5)	1·53	C_{ph}—C_{ph} (mean)	1·40

Discussion. The crystal structure consists of the packing of well-separated monomeric units. Fig. 1 shows a view of the molecule and the numbering system. Bond distances and angles are reported in Tables 2 and 3 respectively, and details of some of the mean planes in Table 4. The O(1)···O(2) and O(3)··· O(4) 'bite' lengths are 2·79 and 2·82 Å. Other structural details also agree well with the values reported (Bandoli *et al.*, 1977) for octahedral *trans*-bis(2,4-pentanedionato) complexes; for instance the dihedral angles between O—Tc—O planes and the ligand mean planes are 7·0 and 10·4°. The molecular structures of the α and β forms are essentially identical; even the three shortest distances [O(4)···C(1)($\bar{x},\bar{y},\bar{z}$), O(2)···C(25)($1-x, \bar{y}, \bar{z}$) and O(3)···C(25)($1-\bar{x}, \bar{y}$,

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33776 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Bond angles* (°) *with e.s.d.'s*

Cl–Tc–P	175·8 (1)	C(3)–C(4)–C(5)	120·0 (9)
O(1)–Tc–O(2)	87·7 (3)	C(5)–C(4)–O(2)	114·4 (8)
O(3)–Tc–O(4)	88·8 (3)	C(3)–C(4)–O(2)	125·6 (8)
Cl–Tc–O(1)	88·4 (2)	O(3)–C(7)–C(6)	115·7 (7)
Cl–Tc–O(2)	89·5 (2)	C(6)–C(7)–C(8)	119·0 (9)
Cl–Tc–O(3)	87·8 (2)	O(3)–C(7)–C(8)	125·2 (9)
Cl–Tc–O(4)	89·5 (2)	C(7)–C(8)–C(9)	124·4 (9)
P–Tc–O(1)	95·4 (2)	C(8)–C(9)–C(10)	119·7 (9)
P–Tc–O(2)	92·3 (2)	O(4)–C(9)–C(10)	114·2 (9)
P–Tc–O(3)	88·4 (2)	C(8)–C(9)–O(4)	126·0 (8)
P–Tc–O(4)	88·5 (2)	Tc–P–C(11)	108·4 (3)
O(1)–Tc–O(4)	93·4 (2)	Tc–P–C(17)	120·6 (3)
O(1)–Tc–O(3)	175·6 (2)	Tc–P–C(23)	112·8 (3)
O(2)–Tc–O(3)	90·0 (3)	C(11)–P–C(17)	101·2 (4)
O(2)–Tc–O(4)	178·6 (3)	C(11)–P–C(23)	105·8 (4)
Tc–O(1)–C(2)	128·4 (6)	C(17)–P–C(23)	106·5 (4)
Tc–O(2)–C(4)	128·3 (5)	P–C(11)–C(12)	116·8 (7)
Tc–O(3)–C(7)	127·2 (5)	P–C(11)–C(16)	122·7 (7)
Tc–O(4)–C(9)	126·7 (6)	P–C(17)–C(18)	119·1 (6)
O(1)–C(2)–C(1)	115·1 (8)	P–C(17)–C(22)	119·6 (7)
C(1)–C(2)–C(3)	120·2 (9)	P–C(23)–C(24)	116·9 (6)
O(1)–C(2)–C(3)	124·7 (10)	P–C(23)–C(28)	122·8 (7)
C(2)–C(3)–C(4)	124·5 (10)	C_{ph}–C_{ph}–C_{ph} (mean)	120·0 (5)

Table 4. *Distances of some atoms from certain planes*

Atoms given in bold type define the plane. Units of distances are 0·001 Å.

Plane 1. **O(1)** –24; **O(2)** 25; **O(3)** –25; **O(4)** 24; Tc 41; C(1) –290; C(2) –206; C(3) –287; C(4) –167; C(5) –237; C(6) –463; C(7) –298; C(8) –407; C(9) –212; C(10) –234

Plane 2. **O(1)** –2; **C(2)** 3; **C(3)** –2; **C(4)** 0; **O(2)** 1; Tc –177; O(3) –473; O(4) –392; C(1) 62; C(5) 31

Plane 3. **O(3)** 8; **C(7)** –5; **C(8)** –10; **C(9)** 20; **O(4)** –13; Tc –261; O(1) –671; O(2) –533; C(6) 34; C(10) 137

Plane 4. **Tc** 181; **O(1)** 88; **O(2)** 155; **O(3)** 141; **O(4)** 174; **C(2)** –108; **C(3)** –190; **C(4)** –54; **C(7)** –117; **C(8)** –225; **C(9)** –45

Dihedral angles (°)

2—3 20·7; C(11)–(16)—C(17)–(22) 68·3; C(17)–(22)—C(23)–(28) 58·7; C(11)–(16)—C(23)–(28) 65·0

Angle between the normal to plane 4 and the least-squares *Chem. Soc. A*, pp. 1837–1844.

$\bar{z}$)] are comparable (3·42, 3·48, 3·51 Å in the α form and 3·34, 3·45, 3·45 Å in the β form, respectively) and the two modifications show normal contact distances.

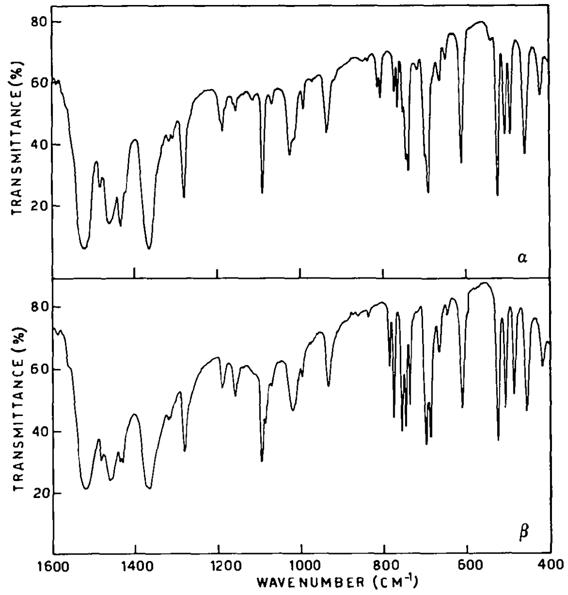

Fig. 2. Infrared spectra of the α and β forms in Nujol mull using KBr windows.

In order to ensure that the two triclinic crystals are not the same crystalline form in two different settings, some tests have been performed. First, the infrared spectra of the two forms are quite similar; nevertheless, there are some differences in the position and intensity of the peaks in the region 700–800 cm^{-1} (Fig. 2). Secondly, it has not been possible to find a transformation between a doubled β cell and the α cell. Third, if the structure described for the α form corresponds to a setting of the β form with a doubled cell, the two 'independent' molecules found in the α structure should have the same orientation. However, the Tc(1)–Cl(1) vector has coordinates –0·1243, –0·1473, 0·0039 and the Tc(2)–Cl(2) vector has 0·1860, 0·0800, 0·0597, which are certainly not parallel. Finally, the closest Tc···Tc separations (7·39 and 7·68 Å in the α and β forms, respectively) are significantly different. All this evidence substantiates our claim for there being two forms of the same compound.

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