Inorganica Chimica Acta, *193* (1992) 167–172

Preparation, characterization and crystal structure of a mixed ligand complex of technetium with DPPE and oxalic acid: oxalato-bis(1,2-bis(diphenylphosphino)ethane)technetium(II)

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(Received December 11, 1990; revised November 11, 1991)

Abstract

Reduction of pertechnetate in hot alcoholic solution with 1,2-bis(diphenylphosphino)ethane in the presence of oxalic acid leads to a mixed ligand complex. Characterization of the compound by elemental analysis, IR, UV–Vis, ^{1}H NMR and mass spectrometry indicates that the oxalic acid ligand coordinates as bidentate. A complete crystal and molecular structure determination, performed on one type of crystal of the paramagnetic oxalato-bis(1,2-bis(diphenylphosphino)ethane)technetium(II), is the first structural characterization of a mixed ligand Tc complex with P and O chelate ligand.

Introduction

The preparation and chemistry of technetium complexes is of considerable interest for the development of organ specific ^{99m}Tc compounds used in nuclear medicine.

Complexes of technetium in different oxidation states with diphosphines and various co-ligands are described in connection with the development of robust cationic technetium complexes for potential use as myocardial imaging agent [1–3]. Tc(III) and Tc(II) form stable mixed ligand complexes with 1,2-bis(diphenylphosphino)ethane (DPPE) and halogens, pseudohalogens and thiole ligands [4–6].

Moreover, Tc(IV)– and Tc(V)–oxalato complexes and a Tc(VI)–nitrido oxalato complex have been described [7, 8].

Lastly phosphine carboxylate complexes of the general formula TcL_3 were developed in which L is a P,O bidentate, tertiary phosphine ligand which contains a pendant carboxylate group [9].

Mixed ligand complexes of Tc with diphosphines and carboxylic acids were unknown up to now. Attempts to form such a complex with DPPE and oxalic acid led to the synthesis of a Tc–DPPE–oxalato complex and its characterization by spectroscopic methods and X-ray diffraction.

Experimental

Materials

Ammonium [^{99}Tc] pertechnetate (0.3 M aqueous solution) was supplied by the Central Institute of Stable Isotopes (Leipzig).

All other chemicals were of analytical grade.

Potassium pertechnetate was obtained by cation exchange of NH_4TcO_4 on H^+-Dowex and addition of an equimolar amount of KOH to the $HTcO_4$ solution.

Preparation of the complex

60 μmol ammonium or potassium pertechnetate were reduced under nitrogen in ethanolic solution (12 ml) containing 500 μmol DPPE and 7 mmol of oxalic acid by heating for 20 min in a boiling water bath. After cooling, dichloromethane (20 ml) and water (20 ml) were added to the orange–red solution. The organic phase containing the complex was separated and washed with water several times in order to remove oxalic acid. When the water phase was neutral (all oxalic acid was separated from the organic phase) the dichloromethane

0020-1693/92/$5.00

solution was dried over sodium sulfate and evaporated under vacuum. The red coloured residue was extracted with benzene to remove excess DPPE and recrystallized from methanol or ethanol. m.p. (decomp.): >180 °C. *Anal.* Found: C, 65.85; H, 5.46; Tc, 9.50. Calc. for $C_{54}H_{48}P_4O_4Tc$: C, 65.92; H, 4.98; Tc, 10.07%.

The stability of the Tc compound under irradiation (X-ray analysis) is attained by adding KPF_6 before crystallization.

Compound characterization

The elemental analyses (except for ^{99}Tc) were performed by the Technical University of Dresden, Chemical Section. Technetium analysis was carried out by liquid scintillation counting. IR spectra were taken on a UR 20 spectrometer in the range 3600–400 cm^{-1} in KBr pellets.

UV–Vis spectra were obtained on a SPECORD M 40 spectrometer. FAB^+ mass spectra were recorded on a VG ZAB-HSQ spectrometer with argon as primary beam gas. The ion gun was operated at 8 kV and 100 μA. Samples were dissolved in glycerol. ^1H NMR spectra were measured on a Bruker Spectrospin WH 90 DS spectrometer at room temperature in CD_3OD and DMSO.

Structure determination

The sample crystallized from a concentrated ethanolic solution contained three different crystal forms named as **I**, **II** and **III**.

Form **I** crystallized in the monoclinic unit cell with cell dimensions of $a = 19.275(15)$, $b = 16.286(7)$ and $c = 19.730(9)$ Å, $\beta = 108.65(5)°$, $V = 5867$ Å^3.

Crystals of **II** are orthorhombic with cell parameters $a = 17.607(4)$, $b = 32.862(7)$ and $c = 19.336(6)$ Å, $V = 11188$ Å^3.

Forms **I** and **II** were unstable under X-ray irradiation. The crystals were destroyed after an exposure time of 15 h. Therefore, the crystal structures could not be determined. In contrast to **I** and **II**, crystals of **III** were stable during the whole exposure time of 100 h.

Crystal data, structure determination and refinement of form III

$C_{54}H_{48}O_4P_4Tc \cdot KPF_6 \cdot 1.5H_2O$: molecular weight 1192.9, triclinic $a = 16.991(13)$, $b = 18.301(8)$, $c = 19.114(12)$ Å, $\alpha = 91.06(4)$, $\beta = 113.07(7)$, $\gamma = 91.25(4)°$, $V = 5465.0$ Å^3; $F(000) = 2440$, $Z = 4$, $D_c = 1.448$ g/cm^3, space group $P\bar{1}$, $\mu(\text{Mo}) = 5.4$ cm^{-1}. The intensity data of a orange–red crystal (size $0.4 \times 0.3 \times 0.5$ mm) sealed in a capillary in water were recorded at room temperature on an automatic Enraf Nonius CAD4-diffractometer with graphite filtered Mo Kα radiation ($\lambda = 0.7107$ Å), using the ω–2θ scan procedure with a variable scan rate of 1.2–6°/min. A total of 10 243 unique reflections was measured up to $2\theta = 40°$; of these 7998 were considered observed ($I(hkl) > 3\sigma(I)$) and were used for structure determination.

The structure was solved by the heavy atom technique. The positions of two symmetry independent technetium atoms were derived from a Patterson map. Subsequent difference Fourier syntheses revealed the positions of all non-hydrogen atoms of the two symmetry independent Tc complexes, two KPF_6 units and three water molecules. Blocked full-matrix least-squares refinement with anisotropic temperature factors assigned to the 'inner core' atoms converged with a conventional R value of 0.125 using unit weight. The oxygen atoms of two water molecules and all fluorine atoms showed very high isotropic temperature factors which can be explained by thermal motion and positional disorder. This may explain the relatively high R value.

Final atomic positional coordinates are listed in Table 1.

Results and discussion

Although complexes of technetium with diphosphines and different co-ligands have been studied intensively, complexes of technetium containing both diphosphines and carboxylic acids have not been described up to now.

This study shows, that the transition metal technetium forms a mixed ligand complex with DPPE and oxalic acid. One type of crystals obtained is stable under irradiation and suitable for structure determination.

Attempts to isolate other mixed ligand complexes with dicarboxylic and hydroxycarboxylic acids like succinic acid, phthalic acid or salicylic acid, citric acid and tartaric acid failed. Most of these complexes are only stable in solution. They decompose if the ligand excess is removed.

Characterization

The reduction of pertechnetate with DPPE in acidic halogenide solutions lead to octahedral coordinated complexes. Besides the favoured Tc(III) complexes $[TcX_2L_2]^+$, neutral Tc(II) complexes $[TcX_2L_2]$ are also observed [4]. With the reducing ligand oxalic acid the Tc(II) complex $Tc(DPPE)_2Ox$ seems to be favoured.

The UV–Vis spectrum shows two absorption maxima at 323 ($\epsilon = 6870$ l mol^{-1} cm^{-1}) and 498.6 ($\epsilon = 1060$ l mol^{-1} cm^{-1}) nm in ethanol. The intensity of the bands suggests charge-transfer transitions [4].

The orange–red crystals are soluble in methanol, ethanol, dichloromethane, acetone, acetonitrile and dimethyl sulfoxide, but insoluble in benzene, chloroform and water. In accordance with this the Tc complex migrates on TLC plates (Kieselgel) with acetone as

TABLE 1. Atomic positional coordinates (with e.s.d.s. in parentheses)

Atom	*x*/*a*	*y*/*b*	*z*/*c*	Atom	*x*/*a*	*y*/*b*	*z*/*c*
Tc	0.55620(8)	0.32435(8)	0.26707(8)	Tc	−0.01218(9)	−0.19346(9)	0.22156(9)
P1	0.6650(3)	0.2603(3)	0.2426(3)	P1	0.1011(3)	−0.2624(3)	0.2126(3)
P2	0.6177(3)	0.2590(3)	0.3857(3)	P2	0.0988(3)	−0.1656(3)	0.3500(3)
P3	0.4507(3)	0.2411(3)	0.1777(3)	P3	0.0113(3)	−0.1044(3)	0.1440(3)
P4	0.4957(3)	0.4035(3)	0.1602(3)	P4	−0.1361(3)	−0.2233(3)	0.1085(3)
O1	0.4802(6)	0.3756(6)	0.3191(6)	O1	−0.0982(7)	−0.1374(8)	0.2587(7)
O2	0.6298(7)	0.4182(6)	0.3257(6)	O2	−0.0617(7)	−0.2732(7)	0.2763(7)
O3	0.4878(7)	0.4626(7)	0.4079(7)	O3	−0.188(1)	−0.1503(9)	0.3182(9)
O4	0.6306(8)	0.5181(7)	0.3923(7)	O4	−0.1482(9)	−0.2935(8)	0.3354(8)
C1	0.705(1)	0.188(1)	0.312(1)	C1	0.203(1)	−0.233(1)	0.292(1)
C2	0.720(1)	0.221(1)	0.393(1)	C2	0.191(1)	−0.222(1)	0.364(1)
C3	0.414(1)	0.279(1)	0.082(1)	C3	−0.058(1)	−0.130(1)	0.044(1)
C4	0.400(1)	0.361(1)	0.087(1)	C4	−0.148(1)	−0.153(1)	0.037(1)
C5	0.516(1)	0.431(1)	0.366(1)	C5	−0.136(1)	−0.173(1)	0.293(1)
C6	0.599(1)	0.4599(9)	0.3621(9)	C6	−0.114(1)	−0.252(1)	0.305(1)
C11	0.766(1)	0.311(1)	0.262(1)	C11	0.099(1)	−0.359(1)	0.230(1)
C12	0.793(1)	0.368(1)	0.313(1)	C12	0.064(1)	−0.386(1)	0.278(1)
C13	0.873(1)	0.401(1)	0.328(1)	C13	0.066(1)	−0.463(1)	0.295(1)
C14	0.929(2)	0.376(1)	0.299(1)	C14	0.101(2)	−0.510(1)	0.261(1)
C15	0.903(2)	0.319(2)	0.248(2)	C15	0.137(2)	−0.485(2)	0.212(2)
C16	0.816(2)	0.280(2)	0.233(2)	C16	0.139(1)	−0.409(1)	0.197(1)
C21	0.648(1)	0.212(1)	0.153(1)	C21	0.129(1)	−0.264(1)	0.131(1)
C22	0.624(1)	0.253(1)	0.087(1)	C22	0.068(1)	−0.292(1)	0.061(1)
C23	0.616(1)	0.219(1)	0.018(1)	C23	0.087(2)	−0.301(2)	−0.005(2)
C24	0.631(1)	0.146(1)	0.013(1)	C24	0.172(2)	−0.280(2)	0.004(2)
C25	0.655(1)	0.105(1)	0.077(1)	C25	0.229(2)	−0.255(2)	0.069(2)
C26	0.663(1)	0.136(1)	0.148(1)	C26	0.212(1)	−0.246(1)	0.135(2)
C31	0.646(1)	0.314(1)	0.472(1)	C31	0.069(1)	−0.183(1)	0.429(1)
C32	0.601(1)	0.305(1)	0.521(1)	C32	0.050(2)	−0.131(2)	0.466(2)
C33	0.621(1)	0.353(1)	0.586(1)	C33	0.010(3)	−0.148(3)	0.520(3)
C34	0.683(2)	0.409(1)	0.601(1)	C34	0.024(2)	−0.220(2)	0.549(2)
C35	0.728(1)	0.416(1)	0.554(1)	C35	0.041(2)	−0.269(2)	0.515(2)
C36	0.710(1)	0.368(1)	0.492(1)	C36	0.069(2)	−0.257(2)	0.454(2)
C41	0.555(1)	0.184(1)	0.398(1)	C41	0.139(1)	−0.072(1)	0.371(1)
C42	0.589(1)	0.115(1)	0.420(1)	C42	0.224(1)	−0.052(1)	0.414(1)
C43	0.532(2)	0.057(1)	0.420(1)	C43	0.251(2)	0.020(2)	0.428(2)
C44	0.448(2)	0.069(1)	0.403(1)	C44	0.190(2)	0.075(2)	0.398(2)
C45	0.414(1)	0.137(1)	0.385(1)	C45	0.106(2)	0.056(2)	0.357(2)
C46	0.466(1)	0.197(1)	0.379(1)	C46	0.078(1)	−0.020(1)	0.342(1)
C51	0.466(1)	0.148(1)	0.155(1)	C51	0.116(1)	−0.083(1)	0.139(1)
C52	0.448(1)	0.120(1)	0.083(1)	C52	0.123(1)	−0.085(1)	0.069(1)
C53	0.459(1)	0.045(1)	0.071(1)	C53	0.203(1)	−0.063(1)	0.066(1)
C54	0.487(1)	−0.001(1)	0.129(1)	C54	0.269(1)	−0.042(1)	0.132(1)
C55	0.506(1)	0.024(1)	0.203(1)	C55	0.261(1)	−0.036(1)	0.203(1)
C56	0.497(1)	0.099(1)	0.219(1)	C56	0.181(1)	−0.059(1)	0.205(1)
C61	0.352(1)	0.231(1)	0.191(1)	C61	−0.026(1)	−0.011(1)	0.150(1)
C62	0.304(1)	0.167(1)	0.173(1)	C62	0.014(1)	0.050(1)	0.131(1)
C63	0.226(1)	0.160(1)	0.184(1)	C63	−0.019(1)	0.119(1)	0.132(1)
C64	0.199(1)	0.218(1)	0.215(1)	C64	−0.085(1)	0.128(1)	0.154(1)
C65	0.245(1)	0.284(1)	0.233(1)	C65	−0.123(1)	0.069(1)	0.175(1)
C66	0.323(1)	0.291(1)	0.223(1)	C66	−0.095(1)	−0.002(1)	0.172(1)
C71	0.460(1)	0.491(1)	0.182(1)	C71	−0.238(1)	−0.224(1)	0.117(1)
C72	0.376(1)	0.494(1)	0.178(1)	C72	−0.278(2)	−0.160(1)	0.120(1)
C73	0.350(2)	0.565(2)	0.196(2)	C73	−0.355(2)	−0.165(2)	0.136(2)
C74	0.402(1)	0.623(1)	0.2178(1)	C74	−0.386(2)	−0.229(2)	0.142(2)
C75	0.484(1)	0.618(1)	0.222(1)	C75	−0.351(2)	−0.291(2)	0.140(2)
C76	0.512(1)	0.551(1)	0.206(1)	C76	−0.273(2)	−0.291(1)	0.126(1)
C81	0.567(1)	0.431(1)	0.114(1)	C81	−0.138(1)	−0.309(1)	0.061(1)
C82	0.650(1)	0.455(1)	0.163(1)	C82	−0.107(1)	−0.371(1)	0.111(1)
C83	0.709(2)	0.472(1)	0.127(1)	C83	−0.106(2)	−0.440(1)	0.073(1)
C84	0.681(2)	0.461(1)	0.048(1)	C84	−0.128(2)	−0.446(2)	−0.004(1)

(*continued*)

TABLE 1. (*continued*)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
C85	0.602(2)	0.434(1)	0.002(1)	C85	−0.157(2)	−0.385(1)	−0.052(1)
C86	0.540(1)	0.417(1)	0.033(1)	C86	−0.162(1)	−0.319(1)	−0.017(1)
K1	0.4141(3)	0.4197(4)	0.5015(3)	K1	0.2755(4)	0.2418(4)	0.6253(3)
P5	0.2073(4)	0.3202(4)	0.4287(4)	P5	0.4949(5)	0.1738(5)	0.6620(7)
F1	0.246(1)	0.381(1)	0.397(1)	F1	0.577(1)	0.212(1)	0.690(1)
F2	0.279(1)	0.339(1)	0.5110(9)	F2	0.530(2)	0.102(1)	0.691(2)
F3	0.269(1)	0.270(1)	0.413(1)	F3	0.404(2)	0.140(1)	0.613(2)
F4	0.178(1)	0.257(1)	0.464(1)	F4	0.459(2)	0.205(2)	0.711(1)
F5	0.143(1)	0.367(2)	0.442(1)	F5	0.460(2)	0.248(2)	0.622(2)
F6	0.142(1)	0.301(1)	0.349(1)	F6	0.508(2)	0.157(2)	0.586(2)
O1W	−0.300(1)	−0.387(1)	0.314(1)				
O2W	−0.236(2)	−0.003(1)	0.283(2)				

eluent with a R_f value of 0.7–0.8, but does not migrate in more polar solvents. The compound does not migrate in electrophoresis with dimethyl sulfoxide or acetonitrile/1% $NaClO_4$ as electrolyte. Attempts to precipitate the complex compound with KPF_6 failed. It seems to be a neutral compound. This is confirmed by conductivity measurements in acetonitrile ($c_{Tc}=2.5\times10^{-4}$ M): $\lambda=3.64$ cm^2 Ω^{-1} mol^{-1}.

The presence of oxalic acid in the complex is evidenced by its IR spectrum. It shows absorptions at 3460, 3070, 2930, 2860, 1690, 1660, 1490, 1440, 1100, 750, 700 and 560 cm^{-1}. The C=O vibrations at 1690 and 1660 cm^{-1} show that both carboxylic groups of oxalic acid are bound to Tc. No vibration can be detected over 1700 cm^{-1} (free COOH group) and between 900 and 1000 cm^{-1} (Tc=O). This is in accordance with the elemental analysis, which corresponds to a ratio of Tc:DPPE:Ox = 1:2:1.

Attempts to prepare a corresponding complex with DMPE (1,2-bis(dimethylphosphino)ethane) failed because of the strong tendency of DMPE and Tc to form the $[Tc(DMPE)_3]^+$ cation in halogenide free solutions [10]. A comparable tris complex with DPPE does not exist because of steric reasons.

The strongly broadened signals of the ^1H NMR spectrum indicate the paramagnetism of the Tc compound.

The FAB$^+$ mass spectra of the Tc–DPPE–oxalato complex are shown in Fig. 1. Besides the molecular ion $Tc(DPPE)_2HOx^+$ ($m/e=984$) the fragmentation product $Tc(DPPE)_2{}^+$ ($m/e=895$) is observed, formed by splitting off the oxalic acid ion Ox^{2-}. Furthermore there are also bi- and trinuclear Tc fragments, as shown in Table 2.

The question whether oligomeric products exist or not could be answered only by a X-ray structural analysis. Unfortunately, the rhombic crystals are unstable in dry air. They decompose to an orange powder within a few hours. Under alcohol or water the Tc complex is stable, but during X-ray irradiation it usually cracks.

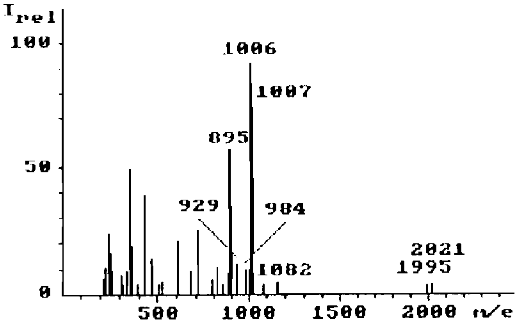

Fig. 1. FAB$^+$ mass spectrum of the $Tc(DPPE)_2Ox$ complex.

TABLE 2. Tc containing fragments observed in the FAB$^+$ mass spectrometry

Fragment[a]	Mass	
	Calculated	Found
$[Tc(DPPE)_2]^+$	895	895
$[Tc_2(DPPE)(M_2PPE)HOx]^+$	929	929
$[Tc(DPPE)_2HOx]^+$	984	984
$[Tc_2(DPPE)(MPPE)HOx]^+$	1006	1006, 1007
$[Tc_2(DPPE)_2Ox]^+$	1082	1082
$[Tc_3(DPPE)(MPPE)_4O]^+$	1995	1995
$[Tc_3(DPPE)_4HOxOH]^+$	1995	1995
$[Tc_3(DPPE)_4OxCOO]^+$	2021	2021

[a] M_2PPE = diphenylphosphinoethane, MPPE = 1-mono,2-diphenylphosphinoethane.

There is a type of crystal that is stable under irradiation conditions found by checking the stability of the Tc compound under irradiation. A perspective view of the neutral compound which includes the atom numbering scheme is shown in Fig. 2. Interatomic bond distances and angles, with e.s.d.s. derived from the refinement, are given in Table 3. There are two symmetry inde-

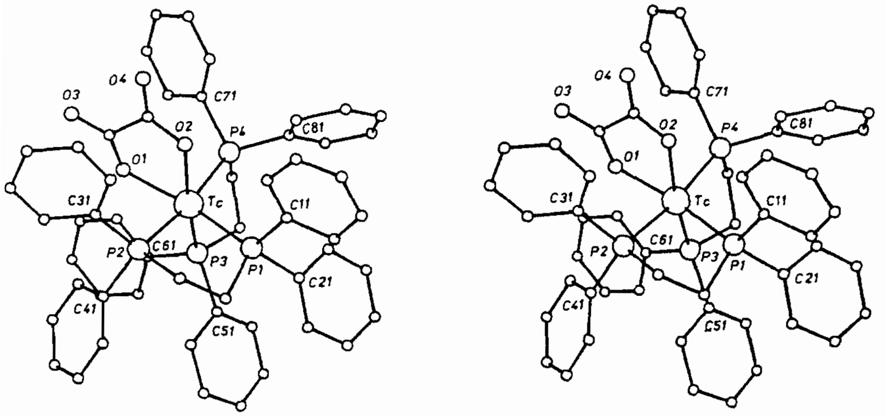

Fig. 2. Stereo plot of one of the $Tc(DPPE)_2Ox$ molecules.

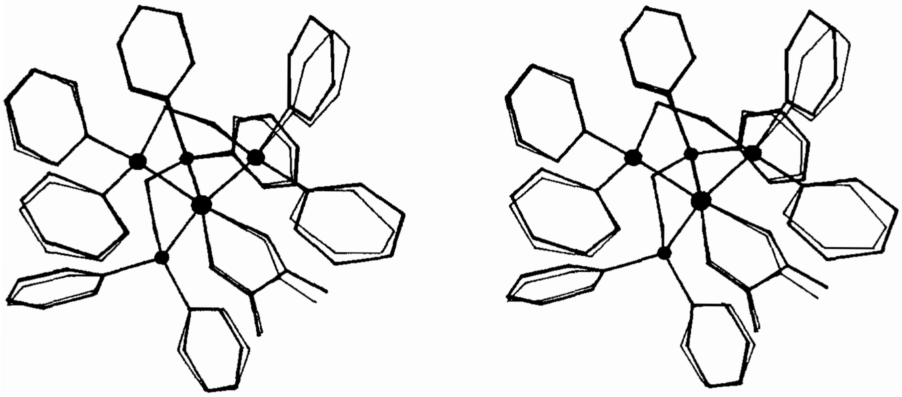

Fig. 3. Superposition of both symmetry independent $Tc(DPPE)_2Ox$ molecules (Tc and P atoms were used for the least-squares fit).

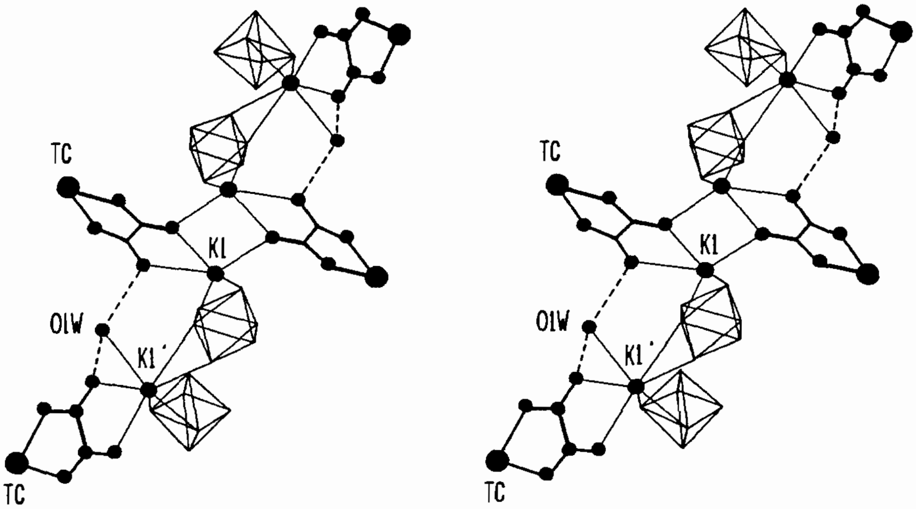

Fig. 4. Crystal structure of form III. Because of clarity only the Tc–oxalato parts of the complexes are shown; O2W and O3W linked to oxalato molecules are left out. The atoms shown in the Figure build up isolated units.

pendent $Tc(DPPE)_2Ox$ molecules in the unit cell. The superposition of both complex molecules is shown in Fig. 3.

The Tc atom is hexacoordinated by four P atoms of the two DPPE ligands and two O atoms of the bidentate bound oxalic acid ligand. Thus, the reducing ligand oxalic acid neutralizes the double positive charged Tc(II) core. This is confirmed by the IR spectrum, mass spectrometry and conductivity measurement.

The single Tc complex molecules are connected by K^+ and PF_6^- ions and form an unusual tetrameric structure presented in Fig. 4.

TABLE 3. Selected interatomic bond distances (Å) and angles (°) with e.s.d.s. in parentheses

Tc–P1	2.408(5)		Tc′–P1′	2.413(5)
Tc–P2	2.442(5)		Tc′–P2′	2.419(5)
Tc–P3	2.404(5)		Tc′–P3′	2.407(5)
Tc–P4	2.423(5)		Tc′–P4′	2.413(5)
Tc–O1	2.14(1)		Tc′–O1′	2.11(1)
Tc–O2	2.12(1)		Tc′–O2′	2.13(1)
P–C	1.83(2)	mean	P′–C′	1.83(3)
O1–C5	1.30(3)		O1′–C5′	1.27(3)
O2–C6	1.27(3)		O2′–C6′	1.28(3)
O3–C5	1.23(3)		O3′–C5′	1.25(3)
O4–C6	1.21(3)		O4′–C6′	1.24(3)
C–C	1.542(9)	mean	C′–C′	1.51(3)
C_{ph}–C_{ph}	1.401(9)	mean	C'_{ph}–C'_{ph}	1.398(8)
P5–F	1.53(3)	mean	P5′–F′	1.5(1)
P2–Tc–P1	80.7(2)		P2′–Tc′–P1′	81.1(2)
P3–Tc–P1	88.8(2)		P3′–Tc′–P1′	88.2(2)
P4–Tc–P1	104.7(2)		P4′–Tc′–P1′	104.8(2)
P3–Tc–P2	105.3(2)		P3′–Tc′–P2′	104.4(2)
P4–Tc–P2	172.2(2)		P4′–Tc′–P2′	172.0(2)
P4–Tc–P3	80.6(2)		P4′–Tc′–P3′	81.5(2)
O1–Tc–P1	165.0(2)		O1′–Tc′–P1′	168.4(3)
O2–Tc–P1	98.8(4)		O2′–Tc–P1′	98.8(4)
O1–Tc–P2	85.2(3)		O1′–Tc′–P2′	88.7(4)
O2–Tc–P2	88.8(4)		O2′–Tc′–P2′	87.6(4)
O1–Tc–P3	99.9(3)		O1′–Tc′–P3′	99.7(4)
O2–Tc–P3	164.9(3)		O2′–Tc′–P3′	167.0(3)
O1–Tc–P4	88.8(3)		O1′–Tc′–P4′	84.9(4)
O2–Tc–P4	84.9(4)		O2′–Tc′–P4′	86.1(4)
O2–Tc–O1	75.6(5)		O2′–Tc′–O1′	75.2(5)
C–P–Tc	109.2(9)	mean	C′–P′–Tc′	109.9(8)
C_{ph}–P–Tc	116.0(9)	mean	C'_{ph}–P′–Tc′	116.4(9)
C21–P1–Tc	124.5(1.0)		C21′–P1′–Tc′	125.2(1.0)
C51–P3–Tc	126.7(1.0)		C51′–P3′–Tc′	125.2(9)
C5–O1–Tc	116.5(1.5)		C5′–O1′–Tc′	117.2(1.7)
C6–O2–Tc	118.0(1.7)		C6′–O2′–Tc′	117.3(1.6)
C_{ph}–C_{ph}–C_{ph}	120.0(1)	mean	C'_{ph}–C'_{ph}–C'_{ph}	120.0(1)

KPF_6 was added to the complex solution to precipitate the supposed complex cation. Despite the fact that the Tc–DPPE–oxalato complex is uncharged, some crystals are formed which are stabilized by insertion of KPF_6 into the crystal lattice. Thus, the resulting tetrameric structure is not necessarily typical of all crystals of the Tc–DPPE–oxalato complex, but it is the unique possibility for stabilizing and determining the crystal structure of this compound by X-ray diffraction.

A Tc–Tc bond could not be found by structure analysis. The di- and trimeric products detected by mass spectrometry are formed either during the analysis by recombination or they exist in the type of crystal which decomposes during irradiation. The average Tc–P bond distances in $Tc(DPPE)_2Ox$ are 2.42(2) and 2.41(1) Å, whereas the Tc(III)–P bond distance reported for $[Tc(DPPE)_2Br_2]^+$ is significantly longer at 2.50(2) Å [4]. In comparison with it the Tc(III)–P bond distance reported for $[Tc(DMPE)_2Cl_2]^+$ is only a little longer at 2.44(2) Å and similar to the Tc–P bond distance determined for $Tc(DPPA)_3$ (2.45(5) Å) [9].

Dependence of the Tc–P bond distance on the oxidation state of Tc for the three Tc–DMPE complexes $[Tc(DMPE)_2(OH)O]^{2+}$, $[Tc(DMPE)_2Cl_2]^+$ and $[Tc(DMPE)_3]^+$ was found [11]: Tc(V)–P = 2.48(1) Å, Tc(III)–P = 2.44(1) Å, Tc(I)–P = 2.40(2) Å. The Tc(II)–P bond distances determined for $Tc(DPPE)_2Ox$ are between the Tc(III)–P and Tc(I)–P bond distances and provide clear evidence for the importance of backbonding in determining the Tc–P bond length in phosphine complexes.

The average Tc–O bond distances in $Tc(DPPE)_2Ox$ are 2.13(2) and 2.12(2) Å. They are somewhat longer than those found in $Tc(DPPA)_3$ (Tc–O = 2.04(2) Å, $[TcO(Ox)_2(HOx)]^{2-}$ (Tc–O = 2.03(4) Å), and $[Tc(Ox)_3]^{2-}$ (Tc–O = 1.99(1) Å).

The C5–O1 and C6–O2 bond distances in the oxalic acid molecule bound to Tc are longer than the others (C5–O3 and C6–O4). This indicates a stretching of the bond distance caused by the electron withdrawing effect of the Tc–O bond. The same effect is reported for the $[Tc(Ox)_3]^{2-}$ anion [7].

Supplementary material

Thermal parameters, and observed and calculated structure factors are available from the authors on request.

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