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Synthesis and X-ray structure of a new Tc(IV) oxalato complex: $K_4[(C_2O_4)_2Tc(\mu\text{-}O)_2Tc(C_2O_4)_2]\cdot 3H_2O$

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Abstract

The synthesis and characterization of the complex $K_4[(C_2O_4)_2Tc(\mu\text{-}O)_2Tc(C_2O_4)_2]\cdot 3H_2O$ by IR, UV–Vis spectroscopy is described; X-ray crystal structure determination is also reported. The complex is dimeric and contains a $Tc(\mu\text{-}O)_2Tc$ unit in which a strong Tc–Tc interaction is present. Crystals are triclinic, space group $P\bar{1}$, $a=8.765(2)$, $b=9.895(2)$, $c=12.822(4)$ Å, $\alpha=87.47(1)°$, $\beta=88.41(1)$, $\gamma=71.03(2)°$, $Z=2$, $V=1050.4$. Each technetium atom is bound to two oxalato anions resulting in an octahedral coordination. From IR data it was possible to assign the frequencies of the ring system vibrations as well for other polyamino–polycarboxylato complexes.

Introduction

There are only two useful synthetic pathways to obtain Tc(IV) complexes: (i) by reduction of pertechnetate salt solutions with Sn(II), SO_2, or other strongly reducing agents, in the presence of a ligand which leads to concomitant complexation, (ii) by direct ligand substitution at a Tc(IV) center using potent ligands such as polyamino–polycarboxylates (PAPC). The first pathway has been widely used in reactions carried out in aqueous media [1, 2]. Moreover, this is the only way to prepare compounds of the short-lived ^{99m}Tc isomer, which is the most widely used isotope in nuclear medicine [3, 4]. On the other hand, direct reactions using the second pathway have not yet been thoroughly investigated due to lack of starting materials which are both readily available and satisfactorily stable towards hydrolysis. As we have recently reported [5], $K_2[TcF_6]$ meets such requirements and it is an appropriate precursor for complexes of Tc(IV). We report here a new complex $K_4[(C_2O_4)_2Tc(\mu\text{-}O)_2Tc(C_2O_4)_2]\cdot 3H_2O$ (1) containing the $Tc(\mu\text{-}O)_2Tc$ moiety: a unit already found both in the EDTA [6] and the NTA [7] complexes. These give in aqueous solution an optical spectrum showing a characteristic maximum at ~500 nm with a molar absorptivity of ~5000. A similar result was also obtained recently using TCTA (TCTA = 1,4,7-triazacyclononane-*N,N′,N″*-triacetate) as ligand [8].

Experimental

Caution: The complex was prepared in several small batches to minimize the risk of severe radioactive contamination.

Synthesis of $K_4[(C_2O_4)_2Tc(\mu\text{-}O)_2Tc(C_2O_4)_2]\cdot 3H_2O$ *(1)*

Ammonium[^{99}Tc]pertechnetate was supplied by the Oak Ridge National Laboratory, Oak Ridge, TN, U.S.A. All other chemicals were obtained from Fluka Chemie AG, CH-9470 Buchs, Switzerland.

The synthesis was carried out using the reaction

$$2K_2[TcF_6]+4K_2(C_2O_4)+5H_2O \xrightarrow[T=80\ °C,\ t=3\ \text{days}\ \ pH=4.3]{} 1+4HF+8KF$$

$K_2[TcF_6]$ was prepared as described in ref. 5. A total of 35.6 mg (0.4 mmol) oxalic acid and 5 ml of a neutral aqueous 0.0114 M solution of $K_2[TcF_6]$ (0.057 mmol) were mixed together in a teflon vial and the pH adjusted to 4.3 by K_2CO_3 addition. The vial was

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TABLE 1 Crystal and experimental data for the X-ray diffraction study

Formula	$C_8H_6K_4O_{21}Tc_2$
Molecular weight	808.55
Crystal dimensions (mm)	0.2×0.2×0.1
Data collection temperature (°C)	22
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.765(2)
b (Å)	9.895(2)
c (Å)	12.822(4)
α (°)	87.47(1)
β (°)	88.41(1)
γ (°)	71.03(2)
V (Å^3)	1050.4
Z	2
ρ (calc.) (g cm^{-3})	2.555
μ (cm^{-1})	
Radiation	Mo K$\bar{\alpha}$ graphite monochromated
λ	0.71069
Measured reflections	$\pm h, \pm k, +l$
θ range (°)	$2.0\ n \leqslant \theta \leqslant 20.0$
Scan type	$\omega/2\theta$
Scan width (°)	$1.0+0.35 \tan \theta$
Max counting time (s)	60
Background time (s)	0.5×scan time
Max scan speed (° min^{-1})	20.5
Prescan rejection limit	0.5 (2σ)
Prescan acceptance limit	0.03 (33σ)
Horizontal receiving slit (mm)	$1.95+\tan \theta$
Vertical receiving slit (mm)	4.0
No. independent data collected	3713
No. observed reflections (n_o) ($\lvert F_o \rvert^2 \geqslant 3\sigma(\lvert F \rvert^2)$)	3260
No. parameters refined (n_v)	38
R^a	0.012
$R_w{}^b$	0.013
GOF^c	1.057

[a] $R=\Sigma \lVert F_o \rvert - 1/k \lvert F_o \rVert / \Sigma \lvert F_o \rvert$ [b] $R_w=[\Sigma w(\lvert F_o \rvert - 1/k \lvert F_o \rvert)^2 / \Sigma w \lvert F_o \rvert^2]^{1/2}$ where $w=[\sigma^2(F_o)]^{-1}$ and $\sigma(F_o)=[\sigma^2(F_o{}^2)+f^2(F_o{}^2)]^{1/2}/2F_o$ with $f=0.045$ [c] $GOF=[\Sigma w(\lvert F_o \rvert - (1/k)\lvert F_o \rvert)^2/(n_o-n_v)]^{1/2}$

tightly closed and left in an oil bath for three days at a temperature of 80 °C. The yield of the reaction was monitored by paper chromatography (R_f 0.25 ± 0.05 in $CH_3CN/H_2O=5/2$). After three days 70% of the hexafluoro complex had transformed into the product, the residual left was either pertechnetate or TcO_2. On addition of ethanol to the cold solution, the inert salt (KF) and oligomers were precipitated. After filtering the volume was reduced to c. 2 ml and subsequent addition of another portion of ethanol caused the remaining inert salt and the byproducts to be precipitated. The filtrate was evaporated to dryness, recrystallization from $EtOH/H_2O=2/1$ yielded 13 mg of dark red crystals (57%). *Anal.* Calc. for $C_8H_6O_{21}K_4Tc_2$: C, 12.13; Tc, 12.48. Found: C, 12.04; Tc, 12.31%.

UV–Vis spectra were recorded on a Uvikon 810 spectrophotometer using 10^{-4} M solutions. $\lambda_{max}=503$ nm, $\epsilon=5930$ M^{-1} cm^{-1}, $\lambda_{max}=248$ nm, $\epsilon=16\,400$ M^{-1} cm^{-1}.

X-ray diffraction

Suitable crystals were obtained by slow evaporation from aqueous solutions. A crystal of approximately prismatic habit was chosen for the data collection and mounted on a glass fiber at a random orientation. A CAD4 diffractometer was used both for the determination of the lattice parameters and for the data collection. Crystal data and experimental parameters are listed in Table 1.

The cell parameters were obtained by least-squares fit of the 2 θ values of 25 high angle reflections using the CAD4 centering routines. A group of three standard reflections were measured every hour to check the stability of the crystal and of the experimental conditions. No significant variation was detected. The crystal orientation was monitored by measuring three standards every 300.

Data was corrected for Lorentz and polarization factors [9] and an empirical absorption correction was applied using azimuthal (ψ) scans of 3 reflections at high χ value ($\chi \geqslant 88.1$). Transmission factors were in the range 0.879–0.996. The standard deviations on intensities were calculated in terms of statistics alone, and an $F_o=0.0$ was given to those reflections having negative net intensities.

The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares. The function minimized was $[\Sigma w(\lvert F_o \rvert - 1/k \lvert F_o \rvert)]^2$ with $w=[\sigma^2(F_o)]^{-1}$.

Anisotropic temperature factors were used for all the atoms but for the hydrogens, which were located on the Fourier difference maps and refined with isotropic thermal factors. Scattering factors were taken from the literature [10] and the contribution of the real and imaginary part of the anomalous dispersion was taken into account [10].

All calculations were carried out using the SDP crystallographic package [9]. Final coordination and equivalent thermal factors are given in Table 2. Bond lengths and bond angles are given in Tables 3 and 4. See also 'Supplementary material'.

Molecular structure of $K_4[(C_2O_4)_2Tc(\mu\text{-}O)_2Tc(C_2O_4)_2]\cdot 3H_2O$

Each of the two technetium atoms in the central $Tc(\mu\text{-}O)_2Tc$ core is coordinated by two oxalato ligands, there is a short Tc–Tc interaction at 2.361(1) Å. It may be noted that a more symmetric geometry,

TABLE 2 Final positional parameters and equivalent thermal parameters with e s d s in parentheses

Atom	x	y	z	B (Å^2)
Tc1	0.27131(2)	0.07319(2)	0.26233(1)	1.332(3)
Tc2	0.01415(2)	0.24337(2)	0.28918(1)	1.335(3)
K1	0.10527(6)	0.27213(6)	−0.06476(4)	2.90(1)
K2	0.43582(6)	0.38543(5)	0.36031(4)	2.242(9)
K3	0.60213(6)	0.35492(5)	0.90621(4)	2.265(9)
K4	−0.18312(6)	−0.02298(5)	0.35785(4)	2.72(1)
O1	0.3694(2)	−0.1463(2)	0.2420(1)	2.21(3)
O2	0.3016(2)	−0.0032(2)	0.4119(1)	2.07(3)
O3	0.5141(2)	0.0602(2)	0.2498(1)	2.04(3)
O4	0.2902(2)	0.1225(2)	0.1083(1)	1.86(3)
O5	−0.2286(2)	0.2659(2)	0.2643(1)	1.90(3)
O6	−0.0203(2)	0.3430(2)	0.1447(1)	2.01(3)
O7	−0.0107(2)	0.1879(2)	0.4406(1)	2.06(3)
O8	−0.0887(2)	0.4431(2)	0.3507(1)	2.22(3)
O9	0.2204(2)	0.2666(1)	0.3029(1)	1.81(3)
O10	0.0648(2)	0.0503(1)	0.2462(1)	1.70(3)
O11	0.4599(2)	−0.3539(2)	0.3288(2)	3.27(4)
O12	0.3700(2)	−0.2006(2)	0.5124(1)	3.15(4)
O13	0.7081(2)	0.0361(2)	0.1294(1)	2.44(3)
O14	0.4521(2)	0.1741(2)	−0.0109(1)	2.40(3)
O15	−0.4282(2)	0.3717(2)	0.1544(1)	2.55(3)
O16	−0.2136(2)	0.4705(2)	0.0378(1)	3.01(4)
O17	−0.0772(2)	0.2752(2)	0.5976(1)	3.16(4)
O18	−0.2002(2)	0.5465(2)	0.4966(2)	3.53(4)
O19W	0.1583(2)	0.5749(2)	0.2126(1)	3.07(4)
O20W	0.1235(2)	0.8711(2)	0.0503(2)	3.63(4)
O21W	0.2305(2)	0.2671(2)	0.7378(2)	4.21(5)
C1	0.3983(2)	−0.2256(2)	0.3263(2)	2.00(4)
C2	0.3541(3)	−0.1409(2)	0.4267(2)	2.08(4)
C3	0.5661(2)	0.0701(2)	0.1554(2)	1.83(4)
C4	0.4294(2)	0.1290(2)	0.0754(2)	1.69(4)
C5	−0.2891(3)	0.3398(2)	0.1817(2)	1.79(4)
C6	−0.1684(3)	0.3913(2)	0.1143(2)	1.93(4)
C7	−0.0683(2)	0.2926(2)	0.5032(2)	2.01(4)
C8	−0.1265(3)	0.4422(2)	0.4487(2)	2.22(4)
H1	0.120(3)	0.606(3)	0.263(2)	2.9(6)*
H2	0.158(4)	0.488(3)	0.220(2)	5.0(8)*
H3	0.198(4)	0.354(4)	0.715(3)	6.4(9)*
H4	0.341(5)	0.245(4)	0.748(3)	9(1)*
H5	0.136(6)	0.929(5)	−0.005(4)	13(2)*
H6	0.126(4)	0.904(4)	0.094(3)	7(1)*

Starred atoms were refined isotropically Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3[a^{2*}B(1,1)+b^{2*}B(2,2)+c^{2*}B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)])$

i e $2/m$ is not observed even though it could be obtained by interchanging the positions of O(5) and O(6) (Fig 1) We note that the observed coordination is consistent with the lowest intramolecular repulsion between the ligands The angles of the bridging oxygens O(9) and O(10) are somewhat larger than those in the corresponding EDTA system (av 76.21(5) and 75.2°, respectively) whereas the bond lengths Tc–O(9) and Tc–O(10) are comparable (1.913 Å) The bond lengths between the oxygens of the oxalato and the technetium atoms are different 2.086(10) and 2.028(9) Å av, respectively, due to the *trans* influence of the bridging oxygen The Tc(μ-O)$_2$Tc four membered ring core is approximately planar while the atoms O(1), O(3), O(5) and O(8) deviate from this plane towards the other carboxylate groups A similar structure to that of **1** has been found in the analogous dimeric Re(IV) oxalato complex [11]

IR Spectroscopy

Although the EDTA and the NTA complexes, which contain a similar four membered ring core have already been described [6, 7], the frequencies of the ring vibrations were not attributed, owing to the overlap of the bands corresponding to the ligand vibrations with those of the Tc(μ-O)$_2$Tc moiety In contrast for compound **1** the corresponding normal modes can easily be assigned The frequencies and stretching force constants for the central ring core are listed in Table 5

The A$_g$ and B$_{3g}$ vibrations are Raman active as well as B$_{1u}$ and B$_{2u}$ are IR active

$$\mathrm{A_g}\quad S_1=\frac{1}{2}(\Delta_1+\Delta_2+\Delta_3+\Delta_4) \tag{1}$$

$$\mathrm{B_{3g}}\quad S_2=\frac{1}{2}(\Delta_1-\Delta_2-\Delta_3+\Delta_4) \tag{2}$$

$$\mathrm{B_{1u}}\quad S_3=\frac{1}{2}(\Delta_1+\Delta_2-\Delta_3-\Delta_4) \tag{3}$$

$$\mathrm{B_{2u}}\quad S_4=\frac{1}{2}(\Delta_1-\Delta_2+\Delta_3-\Delta_4) \tag{4}$$

$$\lambda_1=\{\mu_m(1+\cos(180°-\theta)+\mu_o(1+\cos\theta))\}(k+k_{\mathrm{MOM}}+k_{\mathrm{OMO}}) \tag{5}$$

$$\lambda_2=\{\mu_m(1-\cos(180°-\theta)+\mu_o(1+\cos\theta))\}(k-k_{\mathrm{MOM}}-k_{\mathrm{OMO}}) \tag{6}$$

$$\lambda_3=\{\mu_m(1-\cos(180°-\theta)+\mu_o(1+\cos\theta))\}(k+k_\iota) \tag{7}$$

$$\lambda_4=\{\mu_m(1+\cos(180°-\theta)+\mu_o(1-\cos\theta))\}(k-k_\iota) \tag{8}$$

where μ_m, μ_o reciprocal masses, k bridge M–O force constant, k_{MOM} M–O–M bridge interaction constant, k_{OMO} O–M–O bridge interaction constant, $k_\iota=k_{\mathrm{MOM}}-k_{\mathrm{OMO}}$

Our subsequent calculations of the stretching force constants [12] from the Tc–O–Tc angle and application of the results to the other di-(μ-O) bridged systems allow the determination of the relevant vibration frequencies As the point group of the four membered ring core is D_{2h}, two infrared active normal

TABLE 3 Bond lengths (Å) in compound 1

Tcl	O1	2 085(1)	Tcl	O2	2 023(1)	Tcl	O3	2 091(1)
Tcl	O4	2 028(1)	Tcl	O9	1 911(1)	Tcl	O10	1 914(1)
Tc2	O5	2 098(1)	Tc2	O6	2 042(1)	Tc2	O7	2 020(1)
Tc2	O8	2 069(1)	Tc2	O9	1 908(1)	Tc2	O10	1 918(1)
O1	C1	1 287(3)	O2	C2	1 296(3)	O3	C3	1 293(3)
O4	C4	1 301(3)	O5	C5	1 283(3)	O6	C6	1 294(3)
O7	C7	1 298(3)	O8	C8	1 291(3)	O11	C1	1 207(3)
O12	C2	1 214(3)	O13	C3	1 219(3)	O14	C4	1 210(3)
O15	C5	1 214(3)	O16	C6	1 219(3)	O17	C7	1 219(3)
O18	C8	1 208(3)	C1	C2	1 538(3)	C3	C4	1 547(3)
C5	C6	1 544(3)	C7	C8	1 542(3)	Tcl	Tc2	2 361(1)

TABLE 4 Bond angles (°) in compound 1

Tc2	Tcl	O1	137 85(5)	Tcl	Tc2	O5	138 54(2)
Tc2	Tcl	O2	95 98(6)	Tcl	Tc2	O6	99 60(6)
Tc2	Tcl	O3	140 15(3)	Tcl	Tc2	O7	96 39(4)
Tc2	Tcl	O4	96 14(4)	Tcl	Tc2	O8	139 61(4)
Cl	O1	Tcl	115 9(3)	C5	O5	Tc2	114 9(1)
C2	O2	Tcl	117 0(3)	C6	O6	Tc2	115 4(2)
C3	O3	Tcl	114 8(2)	C7	O7	Tc2	116 1(2)
Tcl	O9	Tc2	76 21(5)	Tcl	O10	Tc2	75 2(3)

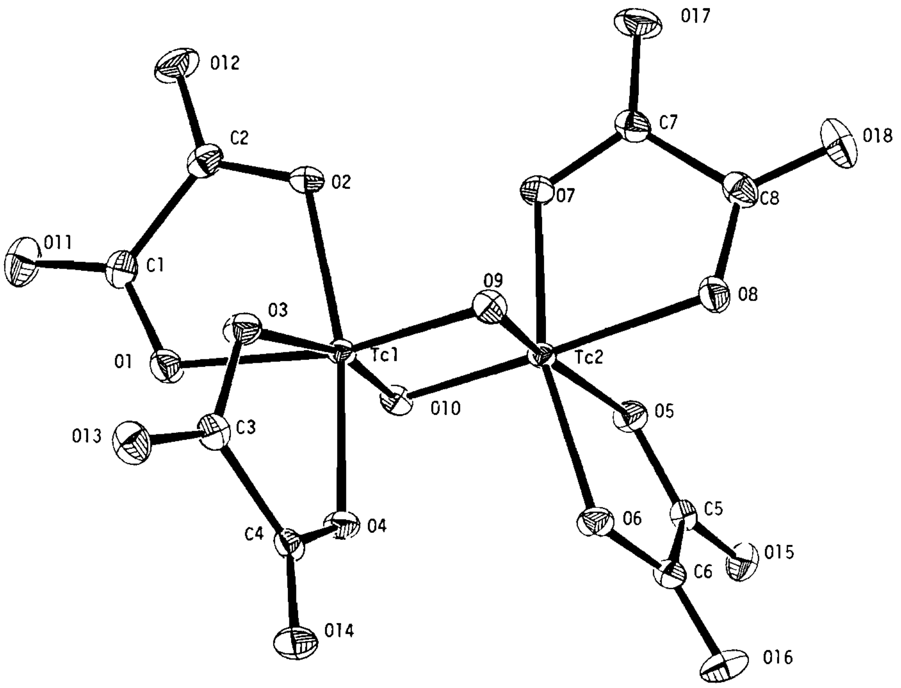

Fig 1 ORTEP of $K_4[(C_2O_4)_2Tc(\mu\text{-}O)_2Tc(C_2O_4)_2]$, thermal ellipsoids are drawn on the 50% level

modes (B_{1u} and B_{2u}) are expected Moreover, due to the frame distortion upon coordination, the two inactive modes (A_g and B_{3g}) may also become weakly active

The data of Table 5 show the influence of ligands on stretching forces in the di-(μ-O) core but more examples are needed in order to find some correlations As already mentioned [7], the M_2O_2 ring

TABLE 5 Stretching frequencies (cm^{-1}) and force constants (mdyn/Å)[a]

Complex	ν_3	ν_4	⟨Tc–O–Tc angle⟩	$k+k_1$	$k-k_1$
Tc–ox	730	401	76 2	3 49	1 71
Tc–EDTA	725	404	75 2	3 39	1 78
Tc–NTA	715	410	76 0	3 34	1 80
Tc–EDDA	715	407	76 4	3 35	1 77

[a] For the calculation of the force constants the symmetry coordinates are given in (1)–(4) and the secular eqns (5)–(8) were used

seems to be a relatively rigid entity whose structure is not easily deformed by ligand with different bonding requirements Application of this method to the recently synthesized $[(\mathrm{EDDA})\mathrm{Tc}(\mu\text{-O})_2\mathrm{Tc})\mathrm{EDDA})]$ complex [13] leads to the conclusion that this complex also has the same dimeric geometry with a four membered ring core (EDDA = ethylenediamine-*N*,*N*′-diacetate)

An attempt to attribute the vibrations was made by Munze and co-workers [14] by substituting the ring ^{16}O with ^{18}O Because of the isotope effect, a displacement in wavelength of the M–O vibrations should occur Therefore the bands at 715 and 555 cm^{-1} were assigned to the ring vibrations Using this assignment for Tc–O–Tc moiety an angle larger than 100° can be calculated while the observed is approximately 75° [6]

The same calculations on the $\mathrm{Mo}(\mu\text{-O})_2\mathrm{Mo}$ complexes [12] show that the interaction between the two molybdenum centers is weaker than in the corresponding technetium systems Consequently the Mo–O–Mo angle should increase, usually being greater than 80°, a relationship between the angle and wavenumber (down to a value of 80°) has also been obtained but it cannot be applied to the analogous technetium systems, where the angles are considerably smaller

Conclusions

The hexahalogenotechnetates(IV) $[\mathrm{TcX}_6]_2{}^{2-}$ ($\mathrm{X} = \mathrm{I}^-$, Br^-, Cl^-) are very sensitive to hydrolysis and are only stable in strong acidic solutions The robust hexafluoro complex $[\mathrm{TcF}_6]^{2-}$ in contrast exists in solution in the pH range 1–14 without any decomposition Indeed at room temperature no reaction took place for weeks, whereas the reaction rate increased quickly with temperature Under these conditions it is impossible to prepare and isolate the possible kinetic intermediates in the reaction pathway One of these intermediates could be the recently reported mononuclear $[\mathrm{Tc}(\mathrm{C}_2\mathrm{O}_4)_3]^{2-}$ complex [15] On the other hand, the complexes that we have prepared are so stable that they can resist high temperature and long reaction times

The moiety $[\mathrm{Tc}(\mu\text{-O})_2\mathrm{Tc}]^{4+}$ normally found in Tc(IV) complexes may be regarded as an hydrolytic species formed from the hypothetical $\mathrm{Tc_{aq}}{}^{4+}$ ion Species of the composition $\mathrm{MO}^{(z-2)-}$ are also known for other metal centers M^{z+} and they are often polymeric This is the case for Tc(IV) Only recently the first monomeric tris(oxalato) complex of Tc^{4+} was isolated, showing that the aqua ion $\mathrm{Tc_{aq}}{}^{4+}$ can also be present in aqueous solution [15]

Supplementary Material

A table of observed and calculated structure factors and an extended list of bond lengths and angles may be obtained from the authors upon request

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