

152. Preparation, Characterization, Crystal and Molecular Structure of $\text{Na}_2[\text{N}(\text{CH}_2\text{COO})_3^{99}\text{Tc}(\text{IV})(\mu\text{-O})_2^{99}\text{Tc}(\text{IV})\text{N}(\text{CH}_2\text{COO})_3] \cdot 6\text{H}_2\text{O}$

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Summary

The title compound and its potassium analog have been prepared from corresponding aqueous solutions of $^{99}\text{TcO}_4^-$ at $\text{pH} \approx 2$ with SO_2 as a reducing agent. An X-ray structure determination of the Na-salt showed Tc coordinated to the tetradentate $\text{N}(\text{CH}_2\text{COO})_3^-$ ligand (NTA). Two Tc-NTA moieties are joined *via* two bridging O-atoms into a four-membered Tc_2O_2 ring. The observed diamagnetism, a strong absorption band at 19950 cm^{-1} , and a short Tc-Tc distance of 2.363 \AA are typical for the Tc_2O_2 -fragment with its strong metal-metal interaction. The structural *trans*-influence at Tc and the network of H-bonds are consistent with Tc in oxidation state IV.

Introduction. – During the last few years ^{99}Tc has become increasingly available from reactor waste. This has led to applications of ^{99}Tc in nuclear medicine and hence to an increased interest in its chemical behaviour in aqueous solutions. The complexes with aminocarboxylate ligands have been the subject of several investigations [1–3].

Tc is commercially available in the form of an aqueous ammonium pertechnetate solution, $\text{NH}_4^{99}\text{Tc}(\text{VII})\text{O}_4$. Complexes containing Tc in lower oxidation states are only stable in the presence of sufficiently strong ligands; no aqua-ion of Tc in any oxidation state has been identified so far. Chelate complexes can be prepared by reducing O_2 -free solutions containing TcO_4^- and the desired ligand. Since TcO_4^- is a rather weak oxidizing agent relatively strong reducing agents are needed.

An alternative route, specifically to Tc(IV)-compounds, is *via* the complex salts $\text{M}_2\text{Tc}(\text{IV})\text{X}_6$ ($\text{M} = \text{Na}^+, \text{K}^+$; $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$). These are easily prepared from NH_4TcO_4 in the corresponding concentrated acid HX . Subsequent ligand exchange tends to be slow and is usually accompanied by the formation of hydrolytic by-products such as TcO_2 [4].

Synthetic methods for preparing Tc-complexes are, in many aspects, similar to those used in corresponding rhenium chemistry [5].

The oxidation state of Tc in the product is usually determined from redox titrations and magnetic susceptibility measurements. In the case of the amino-carboxylate complexes these methods give equivocal results. Therefore a series of crystal structure analyses was undertaken. Preparation, physical and chemical characterization, crystal, molecular and electronic structure of $[\text{H}_2\text{EDTA Tc(IV)}-(\mu\text{-O})_2\text{TcEDTAH}_2] \cdot 5 \text{H}_2\text{O}$ (EDTA = ethylenediaminetetraacetate) have been reported and discussed previously [3]. Here we report the synthesis, chemical and physical properties, crystal and molecular structure of $\text{Na}_2[\text{NTA Tc(IV)}-(\mu\text{-O})_2\text{TcNTA}] \cdot 6 \text{H}_2\text{O}$ (NTA = nitrilotriacetate).

Experimental. – *Cautionary Remark.* The ^{99}Tc -complex was prepared in small batches to minimize the risk of severe radioactive contamination. As a consequence the samples for X-ray analysis, elemental analysis and alkalimetric titration came from different batches.

Preparation. An $\text{NH}_4\text{Tc(VII)O}_4$ -solution (*Oak Ridge National Laboratory*) was passed through a cation exchanger (*Lewatit S 100*) in the H^+ -form; 0.25 mmol $\text{Na}_2\text{NH}(\text{CH}_2\text{COO})_3$ (Na_2HNTA) was dissolved in 10 ml of the resulting 0.01 M HTcO_4 -solution (0.1 mmol) and HClO_4 was added to reach a $\text{pH} \approx 2$. SO_2 was bubbled through the solution at $70\text{--}80^\circ$ during several days. Progress of the reduction was monitored by paper chromatography (solid phase: paper *N. 2043a*, *Schleicher-Schüll*; eluent $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ 70:30 v/v). The reaction was terminated when the chromatogram showed only the desired product ($R_f = 0.35 \pm 0.05$). The solution was then cooled and kept at r.t. to allow slow evaporation of the solvent. The blackish crystals of the Tc-complex were separated mechanically from those of NaClO_4 and H_3NTA . The raw product can be recrystallized from a 0.01 M HClO_4 -solution. The K-salt was obtained in a similar way. Both products are quite hygroscopic.

Analysis. The products were analyzed for ^{99}Tc using a liquid scintillation counter (*Mark II, Nuclear Chicago*, calibrated with a $^{99}\text{TcO}_4^-$ -solution of known concentration. The ^{99}Tc -content of the reference solution was determined gravimetrically with tetraphenylarsonium chloride). Analysis for C, H and N was done in the laboratories of *H. Malissa* and *G. Reuter* (Engelskirchen, Germany). Finally Na and K were determined in the section «Chemie» of the *EIR*, Würenlingen by neutron-activation analysis.

$\text{C}_{12}\text{H}_{12}\text{Na}_2\text{N}_2\text{O}_{14}\text{Tc}_2 \cdot 6 \text{H}_2\text{O}$ (760.1)	Calc.	C 18.96	H 3.18	Na 6.05	N 3.68	Tc 26.0%
	Found	C 19.02	H 2.61	Na 5.8	N 3.68	Tc 26.3%
$\text{C}_{12}\text{N}_{12}\text{K}_2\text{N}_2\text{Tc}_2$ (672.2)	Calc.	C 21.05	H 1.75	K 11.4	N 4.09	Tc 28.9%
	Found	C 21.35	H 1.82	K 11.5	N 4.12	Tc 28.9%

Chemical and Physical Properties. Alkalimetric titrations of the complex anion in presence of HClO_4 show no protonation of the complex. This is as expected because the three carboxylate groups are bound to Tc. Dissociation of the complex takes place slowly at $\text{pH} \approx 0$ (N_2 atmosphere in a glove-box).

Optical spectra between $12,500$ and $50,000 \text{ cm}^{-1}$ were recorded on a (*UNICON 810*) spectrometer from aq. solutions (0.0004 M) in a 10 mm cell. They show a strong band at $19,950 \text{ cm}^{-1}$ ($\epsilon = 5000$) and two poorly resolved bands at $18,800 \text{ cm}^{-1}$ ($\epsilon = 340$) and $24,000 \text{ cm}^{-1}$ ($\epsilon = 380$). Above $30,000 \text{ cm}^{-1}$ the optical density increases continuously.

Magnetic measurements were performed by the *Faraday* method between 77 and 300 K on powdered samples. The small, temperature-independent signal indicated diamagnetism.

$^1\text{H-NMR}$ measurements in D_2O on a *Bruker HX 90 E* instrument show only one peak at 3.5 ppm (rel. to ext. TSP), corresponding to six CH_2 -protons.

X-Ray Diffraction Experiment. Crystal data: $\text{C}_{12}\text{H}_{12}\text{Na}_2\text{N}_2\text{O}_{14}\text{Tc}_2 \cdot 6 \text{H}_2\text{O}$, $M = 760.1$, $d_{\text{calc.}} = 2.134 \text{ g cm}^{-3}$, $\mu = 12.7 \text{ cm}^{-1}$, irregular crystal shape with dimensions 0.1–0.2 mm, triclinic, $a = 6.330$ (1), $b = 9.512$ (2), $c = 11.239$ (4) Å, $\alpha = 64.97$ (2), $\beta = 83.00$ (2), $\gamma = 74.74$ (2)° determined from 21 reflection ($6^\circ < \theta < 13.5^\circ$) on a *CAD4* diffractometer; $P1$, $Z = 1$. Intensity measurements: *CAD4* diffractometer,

MoK α ($\lambda = 0.71069$ Å), graphite monochromator, ω -scan, variable scan speed, maximum scan time 60 s, minimum $\sigma(I)/I = 0.01$, 3119 reflections measured with $\theta \leq 28^\circ$, 2715 unique observations with $I > \sigma(I)$, no absorption correction. After about 90% of the data were measured the crystal decayed within a few minutes. Deterioration of the crystal occurred during automatic, unattended data collection. We therefore cannot offer additional observations which would help to explain this phenomenon. The last 10% of the data were measured on a second specimen. The data from the second crystal were scaled such that $k \langle I(\bar{4}\bar{1}0)_{\text{crystal 2}} \rangle = \langle I(\bar{4}\bar{1}0)_{\text{crystal 1}} \rangle$. The intensity control reflection did not indicate a continuous decay of the crystals investigated.

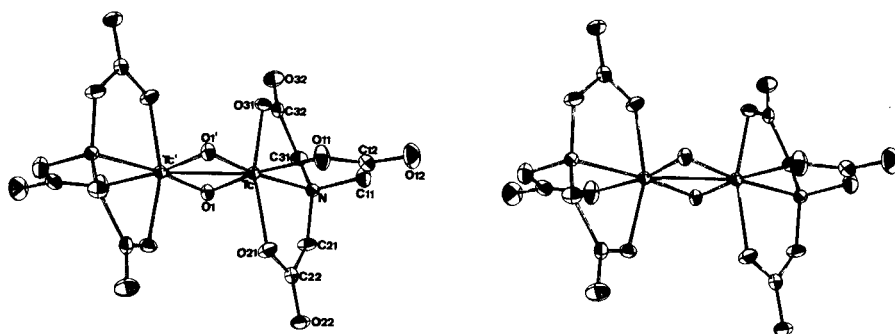


Figure. Stereoscopic drawing of the anion $[NTA Tc(IV)(\mu-O)_2Tc(IV)NTA]^{2-}$ with atomic numbering

Table 1. Positional and Equivalent Isotropic Thermal Parameters^{a)} and their esd's (in terms of least significant digit)^{b)}

Atom	x	y	z	$U_{eq}^a)$
Tc	0.50377 (3)	0.37510 (2)	0.58881 (2)	0.01292 (8)
O1	0.2581 (3)	0.5221 (2)	0.4843 (2)	0.0167 (5)
O11	0.7187 (3)	0.1890 (3)	0.7258 (2)	0.0278 (6)
O12	0.7582 (4)	-0.0475 (3)	0.8946 (2)	0.0368 (7)
O21	0.4075 (3)	0.4485 (2)	0.7365 (2)	0.0218 (6)
O22	0.1434 (4)	0.4545 (3)	0.8854 (2)	0.0284 (6)
O31	0.5405 (3)	0.2418 (2)	0.4826 (2)	0.0210 (5)
O32	0.3379 (4)	0.1436 (3)	0.4032 (2)	0.0290 (7)
N	0.2865 (3)	0.2215 (3)	0.6933 (2)	0.0154 (6)
C11	0.4133 (5)	0.0669 (3)	0.7912 (3)	0.0254 (8)
C12	0.6482 (5)	0.0674 (3)	0.8077 (3)	0.0226 (7)
C21	0.1235 (4)	0.3117 (3)	0.7583 (3)	0.0207 (7)
C22	0.2287 (4)	0.4116 (3)	0.7989 (3)	0.0191 (7)
C31	0.1956 (4)	0.1961 (3)	0.5899 (3)	0.0201 (7)
C32	0.3679 (4)	0.1909 (3)	0.4839 (3)	0.0185 (7)
Na	0.0107 (2)	0.2927 (1)	0.0971 (1)	0.0309 (3)
O2	0.0856 (4)	-0.1665 (3)	0.6799 (2)	0.0361 (7)
O3	0.2939 (5)	0.6929 (4)	0.0174 (3)	0.0484 (8)
O4	0.3513 (5)	0.3463 (4)	0.1411 (3)	0.0455 (8)

a) $U_{eq} = \sum_i \sum_j \beta_{ij} (a_i \cdot a_j) / (6\pi^2)$, cf. [10].

b) Positional coordinates for H-atoms belonging to O2, O3 and O4 have been refined. O–H distances are 0.77, 0.77, 0.71, 0.84, 0.84, 0.88 (7) Å. HOH angles are 108, 105, 104 (7)°.

Structure Analysis and Refinement. The position of the Tc-atom was found from a *Patterson* function; all other non-H-atoms were located from successive *Fourier* syntheses. Full-matrix weighted least-squares refinement was carried out with anisotropic non-hydrogen atoms, and isotropic water H-atoms, but with methylene H-atoms in calculated positions (191 variables). The weighting scheme was $w = x \cdot y$, where $x = y = 1$, except for reflections with $\sin \theta / \lambda \leq 0.35 \text{ \AA}^{-1}$ when $x = \sin \theta / (0.35 \lambda)$ and

Table 2. *Molecular Geometry* (for atom numbering see Fig. 1)^{a)}

a) <i>Averaged coordination geometry of Tc^{b)}</i>			
Tc–N	2.148 (2)	O1–Tc–O <i>i</i> 1	91.1 (1)
Tc–O11	2.072 (2)	O1'–Tc–N	168.8 (1)
Tc–O <i>i</i> 1	2.034 (3)	O1'–Tc–O11	88.5 (1)
Tc–O1(O1')	1.919 (2)	O1'–Tc–O <i>i</i> 1	99.7 (1)
Tc...Tc'	2.363 (2)	N–Tc–O11	80.3 (1)
O1...O1'	3.024 (3)	N–Tc–O <i>i</i> 1	79.8 (1)
O31...O21'	3.005 (3)	O11–Tc–O <i>i</i> 1	86.8 (1)
Tc–O1–Tc'	76.0 (1)	O21–Tc–O31	159.4 (1)
O1–Tc–O1'	104.0 (1)	Tc'–Tc–N	139.3 (1)
O1–Tc–N	87.2 (1)	Tc'–Tc–O11	140.4 (1)
O1–Tc–O11	167.4 (1)	Tc'–Tc–O <i>i</i> 1	98.6 (1)
b) <i>Averaged geometry of chelate rings^{c)}</i>			
N–Ci1	1.492	Ci1–Ci2–O <i>i</i> 1	117.0
Ci1–Ci2	1.523	Ci1–Ci2–O <i>i</i> 2	119.4
Ci2–O <i>i</i> 1	1.298	O <i>i</i> 1–Ci2–O <i>i</i> 2	123.6
Ci2–O <i>i</i> 2	1.222	Ci2–O <i>i</i> 1–Tc	115.9
Tc–N–Ci1	106.3	Ci1–N–C(<i>i</i> +1)	112.5
N–Ci1–Ci2	111.7		
c) <i>Coordination geometry at Na^{d)}</i>			
Na–O2 (1)	2.359 (3)	Na–O12 (3)	2.376 (3)
Na–O3 (2)	2.389 (4)	Na–O22 (4)	2.427 (3)
Na–O4	2.491 (1)	Na–O22 (5)	2.415 (3)
O2–Na–O3	103.6 (1)	average	2.410
O2–Na–O4	95.2 (1)	O3–Na–O22 (5)	86.5 (1)
O2–Na–O12	90.3 (1)	O4–Na–O12	84.9 (1)
O2–Na–O22 (4)	87.4 (1)	O4–Na–O22 (4)	80.6 (1)
O2–Na–O22 (5)	167.6 (1)	O4–Na–O22 (5)	74.2 (1)
O3–Na–O4	160.4 (1)	O12–Na–O22 (4)	165.0 (1)
O3–Na–O12	100.2 (1)	O12–Na–O22 (5)	95.1 (1)
O3–Na–O22 (4)	94.8 (1)	O22 (4)–Na–O22 (5)	84.5 (1)
d) <i>H-bonds^{d)}</i>			
O2...O31 (3)	2.934 (3)	O4...O3	2.924 (5)
O2...O32 (1)	2.870 (4)	O4...O32	2.761 (3)
O3...O4 (6)	2.739 (4)	O3...O21'	3.134 (7)

a) Primed atoms are related to unprimed atoms by the transformation (1-x, 1-y, 1-z); distances in Å angles in deg.

b) Averaged over $i = 2$ and $i = 3$.

c) Averaged over $i = 1$, $i = 2$ and $i = 3$; $(i + 1) \pmod{3}$.

d) O-coordinates obtained from Table 1 with symmetry transformation given in brackets. 1: (\bar{x} , \bar{y} , 1-z) 2: (\bar{x} , 1-y, \bar{z}), 3: (1-x, \bar{y} , 1-z), 4: (\bar{x} , 1-y, 1-z), 5: (x, y, z-1), 6: (1-x, 1-y, z).

for those with $k \cdot F_{\text{obs}} \geq 20$ when $y = 20/(k \cdot F_{\text{obs}})$. Real and imaginary scattering factors were used for neutral atoms [6]. $R = 0.026$, $R_w = 0.031$. Residual electron density close to Na and Tc was $\leq 0.35 \text{ e}\text{\AA}^{-3}$. All calculations were performed with the X-RAY 72 system of programs [7].

Results are given in Tables 1 and 2 as well as in Figure 1. H-positions, anisotropic vibrational parameters and structure factor listings are available from H. B. B. on request.

Discussion. – The molecule $[\text{NTA Tc}(\mu\text{-O})_2\text{Tc NTA}]^{2-}$ shows a central four-membered Tc_2O_2 -ring. Each Tc is also coordinated to the N-atom and to three carboxylate O-atoms of an NTA-ligand (Fig. 1). The molecule shows approximate $2/m$ symmetry, the mirror plane coinciding with the Tc_2O_2 -ring, the molecular inversion center is required by space-group symmetry. The Tc...Tc distance is 2.36 Å and the O...O distance 3.02 Å. An M_2O_2 four-membered ring is also found in $[\text{H}_2\text{EDTA M(IV)}(\mu\text{-O})_2\text{M(IV)EDTAH}_2]$ (M = Tc, Re) [3] [8] and $[\text{ox}_2\text{Re(IV)}(\mu\text{-O})_2\text{Re(IV)ox}_2]^{4-}$ (ox = oxalate) [9] with M...M distances of 2.33, 2.34, 2.36 Å and O...O distances of 3.03, 3.06, 3.07 Å. It seems to be a relatively rigid entity whose structure is not easily deformed by ligands with different bonding requirements.

Distances and angles at Tc averaged according to the approximate symmetry are given in Table 2. They are very similar to the analogous values in $[\text{H}_2\text{EDTA Tc(IV)}(\mu\text{-O})_2\text{Tc(IV)EDTAH}_2]$. The Tc-O11 distance in the molecular plane (2.07 Å) is substantially longer than the Tc-O1 distances in the four-membered ring (1.92 Å) and longer than the Tc-O21 and Tc-O31 distances (average 2.03 Å). This indicates a *trans*-influence on O11 of $\approx 0.05 \text{ \AA}$ by O1. An analogous *trans*-influence of the same magnitude is found for $[\text{ox}_2\text{Re(IV)}(\mu\text{-O})_2\text{Re(IV)ox}_2]^{4-}$.

The similarity in molecular structure among the Tc- and Re-complexes mentioned above is paralleled by similarity in electronic spectra. The optical absorption spectrum of $[\text{NTA Tc(IV)}(\mu\text{-O})_2\text{Tc(IV)NTA}]^{2-}$ shows an intense electronic transition at $19,950 \text{ cm}^{-1}$ ($\epsilon = 5000$), practically the same as for $[\text{H}_2\text{EDTA Tc(IV)}(\mu\text{-O})_2\text{Tc(IV)EDTAH}_2]$ ($20,200 \text{ cm}^{-1}$, $\epsilon = 4000$)¹⁾.

These structural and spectral similarities indicate the same oxidation state in all these compounds. We have given structural arguments for Tc(IV) in $[\text{H}_2\text{EDTA Tc}(\mu\text{-O})_2\text{Tc EDTAH}_2]$ elsewhere [3]. By analogy and also from the stoichiometry we would expect Tc(IV) in $\text{Na}_2[\text{NTA Tc}(\mu\text{-O})_2\text{Tc NTA}] \cdot 6 \text{ H}_2\text{O}$ as well. Of course there is always the possibility that we have interpreted to many or to few acidic protons into the experimentally determined electron density distribution. In the first case the oxidation state of Tc would be lower and in the second case higher (electron neutrality). However, the identification of O2, O3 and O4 as belonging to H_2O -molecules does give a reasonable network of H-bonds, corresponding to the six short O...O distances listed in Table 2. There are no other O...O contacts $< 3.2 \text{ \AA}$. Thus, at least, there is no evidence contradicting a Tc(IV) oxidation state.

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¹⁾ In [3] ϵ was given as 2000, i.e. per Tc, rather than per binuclear complex ion.

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