



A redetermination of the structure of tetraethylammonium *mer*-oxidotrichlorido(thenoyltrifluoroacetylacetonato- κ^2 -O,O')niobate(V)

by R. Koen, A. Roodt and H. Visser

Synopsis

The tetraethylammonium salt of the mono-anionic coordination compound *mer*-oxidotrichlorido(thenoyltrifluoroacetylacetonato- κ^2 -O,O')niobate(V) (NEt₄)[NbOCl₃](tfa), has been prepared under aerobic conditions and characterized by single-crystal X-ray diffraction. (NEt₄)[NbOCl₃](tfa) crystallized in the monoclinic *P*2₁/*c* space group, with *a* = 11.483 (5), *b* = 12.563 (5), *c* = 17.110(5) Å, and β = 100.838 (5)°. The complex structure exists in a 50.0% (*Nb*^A) : 50.0% (*Nb*^B) positional disorder ratio.

Keywords

Bidentate, niobium(V), disorder.

Introduction

Complexes containing organometallic type β -diketone ligands with O,O and O,N donor atoms are used widely in coordination chemistry and have applications in catalysis, radiopharmaceuticals, *etc.* (Schutte *et al.*, 2011; Roodt, Visser and Brink, 2011; Brink *et al.*, 2010; Otto *et al.*, 1998). These ligand systems are very useful because of their highly coordinative nature, high solubility, and also due to their ability to be functionalized with various substituents on the carbonyl carbon atoms (Schutte *et al.*, 2011).

Only a small number of β -diketonate ligands have successfully been coordinated to a Nb(V) metal centre, with only a select few being characterized by X-ray crystallography (Viljoen, 2009; Bullen, Mason and Pauling, 1965; Preuss, Lamding and Mueller-Becker, 1994; Funk, 1934; Davies, Leedlam and Jones, 1999; Allen, 2002). The synthesis and crystal structure determination at room temperature of *mer*-oxidotrichlorido(thenoyltrifluoroacetylacetonato- κ^2 -O,O')niobate(V) {(NEt₄)[NbOCl₃](tfa)} was first reported by Daran *et al.* in 1979. Accordingly, for this current investigation, (NEt₄)[NbOCl₃](tfa) was re-evaluated at 100 K to determine if the structural features might change with temperature.

This study of this structure forms part of an AMI-funded programme to better understand the solid-state characteristics of Ta(V) and Nb(V) complexes and the influences

of the electron-donating and -withdrawing groups of the β -diketone on the activity induced and reaction mechanisms at these metal centres.

Experimental

Materials and instruments

All chemicals used for the synthesis and preparation of the complexes were of analytical grade and were purchased from Sigma-Aldrich, South Africa.

The ¹H-, ¹³C-, and ¹⁹F FT-NMR solution-state spectra were recorded on a Bruker AVANCE II 600 MHz (¹H: 600.28 MHz; ¹³C: 150.96 MHz; ¹⁹F: 564.83 MHz) or Bruker DPX 300 MHz (¹H: 300.13 MHz; ¹³C: 75.47 MHz; ¹⁹F: 282.40 MHz) nuclear magnetic resonance spectrometer using the appropriate deuterated solvent. Chemical shifts, δ , are reported in ppm. ¹H NMR spectra were referenced internally using residual protons in the deuterated solvents, Acetonitrile-*d*₃ [CD₃CN = 1.94(5) ppm]. ¹³C NMR spectra were similarly referenced internally to the solvent resonance [CD₃CN = 1.39(4) ppm and 118.69(8) ppm] with values reported relative to tetramethylsilane (δ 0.0 ppm).

The X-ray intensity data was collected on a Bruker X8 ApexII 4K Kappa CCD area detector diffractometer, equipped with a graphite monochromator and MoK α fine-focus sealed tube (λ = 0.71069 Å, T = 100(2) K) operated at 2.0 kW (50 kV, 40 mA). The initial unit cell determinations and data collection were done by the SMART (Bruker, 1998a) software package. The collected frames were integrated using a narrow-frame integration algorithm and reduced with the Bruker SAINT-Plus and XPREP software package (Bruker, 1999)

* Department of Chemistry, University of the Free State, South Africa.

© The Southern African Institute of Mining and Metallurgy, 2015. ISSN 2225-6253. Paper received Aug. 2015 and revised paper received Aug. 2015.

Tetraethylammonium *mer*-oxidotrichlorido(thenoyltrifluoroacetato- κ^2 -O,O')niobate(V)

respectively. Analysis of the data showed no significant decay during the data collection. The data was corrected for absorption effects using the multi-scan technique SADABS Bruker, 1998b) and the structure was solved by the direct methods package SIR97 (Altomare *et al.*, 1999) and refined using the WinGX (Farrugia, 1999) software incorporating SHELXL (Sheldrick, 1997). The final anisotropic full-matrix least-squares refinement was done on F². The aromatic protons were placed in geometrically idealized positions (C–H = 0.93 – 0.98 Å) and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(C). Non-hydrogen atoms were refined with anisotropic displacement parameters. The graphics were obtained with the DIAMOND program (Brandenburg, 2006) with 50% probability ellipsoids for all non-hydrogen atoms.

Synthesis of (NEt₄)[NbOCl₃(tffa)] (1)

(Et₄N)[NbCl₆] (0.500 g, 1.147 mmol) was added to 4,4-trifluoro-1(2-thienyl)-1,3-butanedione (tffaH) (0.327 g, 1.147 mmol) in acetonitrile (20 cm³). The resulting solution was heated to 50°C and stirred for 30 minutes. The excess solvent was evaporated and dark yellow plate-like crystals of the title compound (1), suitable for X-ray diffraction, were obtained (0.565 g, yield 89 %). IR (ATR, cm⁻¹): $\nu_{\text{(Nb=O)}} = 952$. ¹H NMR (300.13 MHz, Acetonitrile-*d*₃, ppm): $\delta = 5.88$ (s, 1H), 6.83 (m, 1H), 6.93 (dd, 1H), 7.40 (dd, 1H). ¹³C NMR (75.47 MHz, Acetonitrile-*d*₃, ppm): $\delta = 30.1, 118.8, 123.9, 130.0, 137.4, 142.0, 182.3$. ¹⁹F NMR (564.83 MHz, Acetonitrile-*d*₃, ppm): -73.37 .

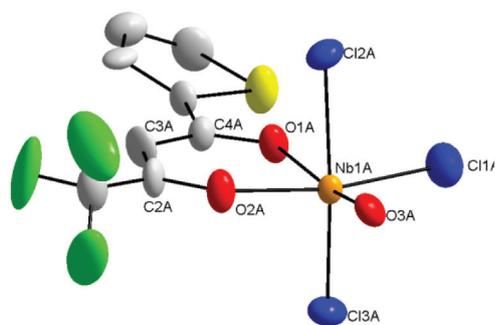


Figure 1 – Graphic illustration of the *mer*-[NbOCl₃(tffa)] anion showing general numbering of atoms. Numbering of the disordered complex denoted by A = 50.0%. The displacement ellipsoids are drawn at 50% probability displacement level. Hydrogen atoms and counter-ion omitted for clarity

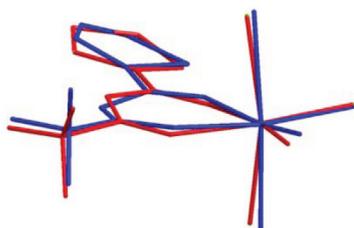


Figure 2 – Graphic illustration of the *mer*-[NbOCl₃(tffa)] anion illustrating the disorder in an overlay. (red) Nb^A = 50.0%; (blue) Nb^B = 50.0%. Hydrogen atoms and counter-ion omitted for clarity

Results and discussion

The title compound was previously prepared by Daran *et al.* (1979), with X-ray diffraction data collected at room temperature. For this study, the reaction was modified as described above and the data collected at 100 K.

The compound crystallizes in the monoclinic space group, *P*2₁/*c*, with four molecules in the unit cell (*Z* = 4). The asymmetric unit consists of a Nb(V) metal centre surrounded by three crystallographically independent chlorido groups (Cl1A – Cl3A), an oxido (O3A) and one *O,O'*-bonded thenoyltrifluoroacetato ligand and a tetraethylammonium cation. A graphic illustration is shown in Figure 1. The complex molecule and the counter-ion are disordered over two positions in a 50 *Nb*^A: 50 *Nb*^B ratio as shown in Figure 2. General crystallographic details are presented in Table I, while selected bond lengths and bond angles are listed in Tables II and III respectively.

A distorted octahedral geometry is displayed for *Nb*^A and *Nb*^B. The Nb-Cl axial distances for NbA vary between 2.428(1) and 2.507(1) Å and the Nb1A-Cl1A and Nb1A-O3A have distances of 2.390(1) and 1.733(1) Å, respectively. When comparing Nb1A-O1A and Nb1A-O2A bond lengths, distances of 2.357(1) vs. 2.037(1) Å are observed. This difference is due to the effects of the electron withdrawing, CF₃ substituent on the bidentate ligand backbone causing a longer NbA-O1A bond length. The *trans* Cl2-Nb1-Cl3 angle is 168.11(1)°, while the O1-Nb1-O2 bite angle is 79.65(1)°. A similar distortion is observed for *Nb*^B, with bond- lengths and angles in accordance with *Nb*^A.

The coordination plane constructed through Cl1A, Cl2A, Cl3A, and O2A, as indicated in Figure 3, shows the niobium metal centre is slightly shifted out of this plane by 0.2751(3) Å.

The molecular packing within the unit cell is illustrated in Figure 4. The packing illustrates a 'head-to-tail' arrangement

Table I

Crystallographic and refinement details of the title compound

Crystallographic data	(NEt ₄)[NbOCl ₃ (tffa)]
Empirical formula	C ₁₆ H ₂₄ F ₃ N ₁ Nb ₁ O ₃ S
Formula weight	566.68
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
a, b, c (Å)	11.483(5), 12.563(5), 17.110(5)
α, β, γ (°)	90.000, 100.838(5), 90.000
Volume (Å ³), <i>Z</i>	2424.3(16), 4
Density (calculated) (mg/m ³)	1.553
Crystal colour, crystal size (mm ³)	Yellow, 0.99 × 0.79 × 0.31
Absorption coefficient μ (mm ⁻¹)	0.951
Theta range, F(000)	2.664 – 27.99°, 1144
Index ranges	-16 ≤ h ≤ 15, -15 ≤ k ≤ 15, -22 ≤ l ≤ 22
Reflections collected, independent reflections, R _{int}	5834, 5209, 0.0574
Completeness (%)	99.6
Max. and min. transmission	0.750 and 0.412
Data, restraints, parameters	5834, 894, 501
Goodness-of-fit on F ²	1.0980
Final R indices [I > 2σ(I)]	R ₁ = 0.0260 wR ₂ = 0.0740
R indices (all data)	R ₁ = 0.0303 wR ₂ = 0.0796
Largest diff. peak and hole (e.Å ⁻³)	0.58, -0.58

Tetraethylammonium *mer*-oxidotrichlorido(thenoyltrifluoroacetato- κ^2 -O,O')niobate(V)

Table II

Selected bond lengths of the two disordered parts in the title compound *mer*-[NbOCl₃(tffa)] anion, denoted by *Nb^A* and *Nb^B*

<i>Nb^A</i>		<i>Nb^B</i>	
Atoms	Bond length (Å)	Atoms	Bond length (Å)
Nb1A-Cl1A	2.390(1)	Nb1B-Cl1B	2.389(1)
Nb1A-Cl2A	2.507(1)	Nb1B-Cl2B	2.373(1)
Nb1A-Cl3A	2.428(1)	Nb1B-Cl3B	2.339(1)
Nb1A-O1A	2.357(1)	Nb1B-O1B	2.254(1)
Nb1A-O2A	2.037(1)	Nb1B-O2B	2.095(1)
Nb1A-O3A	1.733(1)	Nb1B-O3B	1.745(1)

Table III

Selected bond angles of the two disordered parts in the title compound *mer*-[NbOCl₃(tffa)] anion, denoted by *Nb^A* and *Nb^B*

<i>Nb^A</i>		<i>Nb^B</i>	
Atoms	Bond angle (°)	Atoms	Bond angle (°)
O1A-Nb1A-O2A	79.65(1)	O1B-Nb1B-O2B	76.82(1)
Cl1A-Nb1A-O3A	96.28(1)	Cl1B-Nb1B-O3B	103.50(2)
O1A-Nb1A-O3A	171.69(2)	O1B-Nb1B-O3B	166.36(2)
Cl1A-Nb1A-O2A	163.58(1)	Cl1B-Nb1B-O2B	166.38(1)
Cl2A-Nb1A-Cl3A	168.11(1)	Cl2B-Nb1B-Cl3B	160.12(1)
C2A-C3A-C4A	120.60(2)	C2B-C3B-C4B	120.99(2)

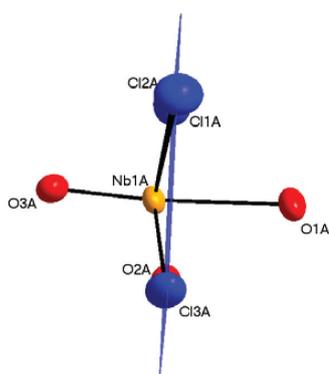


Figure 3 – Side view of the axial plane illustrating the out-of-plane distortion. Displacement ellipsoids are drawn at the 50% probability level

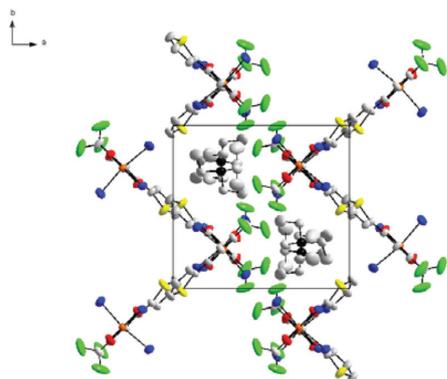


Figure 4 – Packing of (NEt₄)[NbOCl₃(tffa)] (*Nb^A*) along the *c*-axis. Displacement ellipsoids are drawn at the 50% probability level

when viewed along the *c*-axis. There are no classical hydrogen bonds or interactions observed in this structure.

In Figure 5, two coordination planes are illustrated; the first one constructed through O1A, O2A, and Nb1A, and the second through O1A, C2A, C3A, C4A, and O2. The angle between planes revealed the slight, 1.677° out-of-plane bend of the coordinated *O,O'*-bonded thenoyltrifluoroacetato ligand. This also contributes to the distorted octahedral geometry.

The crystal structure determination of the published complex was performed at room temperature (298 K), while the synthesized analogue (1) was determined at 100(2) K. Data obtained for the title compound (1) correlates well with the previously published structure (Daran *et al.* 1979). The disordered part denoted by *Nb^B* differs less from the published structure and is probably a better representation of the anionic complex. Table IV illustrates a comparison between bond angles and distances of the published structure vs. the structure collected at 100K. The greatest difference

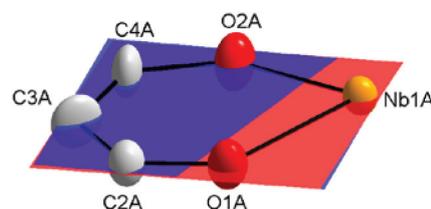


Figure 5 – Illustration of the out-of-plane bend of the coordinated *O,O'*-bonded thenoyltrifluoroacetato ligand. Displacement ellipsoids are drawn at the 50% probability level

Tetraethylammonium *mer*-oxidotrichlorido(thenoyltrifluoroacetato-κ²-O,O')niobate(V)

Table IV

Comparison of bond lengths and bond angles of (NEt₄)[NbOCl₃(tffa)] (Bullen, Mason, and Pauling, 1965) collected at room temperature vs. (NEt₄)[NbOCl₃(tffa)] at 100 K

(NEt ₄)[NbOCl ₃ (tffa)]-Nb ^A (100 K)			(NEt ₄)[NbOCl ₃ (tffa)] (298 K)	
Atoms	Bond length (Å)		Atoms	Bond length (Å)
	Nb ^A	Nb ^B		
Nb1-Cl1	2.390(1)	2.389(1)	Nb1-Cl1	2.367(1)
Nb1-Cl2	2.507(1)	2.373(1)	Nb1-Cl2	2.365(2)
Nb1-Cl3	2.428(1)	2.339(1)	Nb1-Cl3	2.422(2)
Nb1-O1	2.357(1)	2.254(1)	Nb1-O1	2.285(3)
Nb1-O2	2.037(1)	2.095(1)	Nb1-O2	2.044(3)
Nb1-O3	1.733(1)	1.745(1)	Nb1-O3	1.704(3)
Atoms	Bond angle (°)		Atoms	Bond angle (°)
	Nb ^A	Nb ^B		
O1-Nb1-O2	79.65(1)	76.82(1)	O1-Nb1-O2	78.7(1)
Cl2-Nb1-Cl3	168.11(1)	160.12(1)	Cl2-Nb1-Cl3	165.0(1)
C2-C3-C4	120.60(2)	120.99(2)	C2-C3-C4	122.9(1)

between the two complexes is the positional disorder observed in the newly synthesized product.

Conclusions

A simplified method to obtain (NEt₄)[NbOCl₃(tffa)] in aerobic conditions is reported. This highlights the misrepresentation of the 'extreme sensitivity' of niobium(V) complexes to air and water. Clearly, the exclusion of oxygen is not that important, while the exclusion of water is, since it will increase hydrolysis and thus the loss of chloride in favour of aqua, hydroxide, or oxo coordination. The crystallographic investigation revealed that this structure exhibited a 50:50 positional disorder. The electron withdrawing effects of the CF₃ substituent on the bidentate ligand backbone is illustrated by the longer Nb-O bonds of Nb1A-O1A and Nb1B-O1B vs. Nb1A-O2A and Nb1B-O2B. All bond lengths and angles of the complex were found to be in accordance with similar structures in the literature.

Acknowledgements

Financial assistance from the Advanced Metals Initiative (AMI) of the Department of Science and Technology (DST) of South Africa, through the New Metals Development Network (NMDN) managed by the South African Nuclear Energy Corporation Limited (Necsa) is gratefully acknowledged. Gratitude is also expressed towards SASOL, PETLabs Pharmaceuticals, and the University of the Free State for financial support of this research initiative outputs. Furthermore, this work is based on research supported in part by the National Research Foundation of South Africa (UIDs 71836 and 84913).

References

ALLEN, F.H. 2002. Cambridge Structural Database (CSD) Version 5.35, November 2013 update. *Acta Crystallographica*, vol. B58. pp. 380-388.

ALTOMARE, A., BURLA, M.C., CAMALLI, M., CASCARANO, G.L., GIACOVAZZO, C., GUAGLIARDI, A., MOLITERNI, A.G.G., POLIDORI, G., and SPAGNA, R. 1999. SIR97: a new tool for crystal structure determination and refinement *Journal of Applied Crystallography*, vol. 32. pp. 115-119.

BRANDENBURG, K. 2006. DIAMOND, Release 3.0e. Crystal Impact GbR, Germany.

BRINK, A., ROODT, A., STEYL, G., and VISSER, H.G. 2010. Steric vs. electronic anomaly observed from iodomethane oxidative addition to tertiary phosphine modified rhodium(I) acetylacetonato complexes following progressive phenyl replacement by cyclohexyl [PR₃ = PPh₃, PPh₂Cy, PPhCy₂ and PCy₃]. *Dalton Transactions*, vol. 39. pp. 5572-5578.

BRUKER AXS Inc. 1998a. Bruker SMART-NT Version 5.050, Area-Detector Software Package. Madison, WI, USA.

BRUKER AXS Inc. 1998b. Bruker SADABS Version 2004/1, Area Detector Absorption Correction Software. Madison, WI, USA.

BRUKER AXS Inc. 1999. Bruker SAINT-Plus Version 6.02 (including XPREP), Area-Detector Integration Software. Madison, WI, USA.

BULLEN, G.J., MASON, R., and PAULING, P. 1965. The crystal and molecular structure of bis(acetylacetonato)nickel (II). *Inorganic Chemistry*, vol. 4. pp. 456-462.

DARAN, J., JEANIN, Y., GUERCHAIS, J.E., and KERGOAT, R. 1979. The crystal structure of tetraethylammonium trichlorooxo(1,1,1-trifluoro-4-thenoyl-2,4-butanedionato)niobate(V). *Inorganica Chimica Acta*, vol. 33. pp. 81-86.

DAVIES, H.O., LEEDLAM, T.J., and JONES, A.C. 1999. Some tantalum(V) β-diketonate and tantalum(V) aminoalcoholate derivatives potentially important in the deposition of tantalum-containing materials. *Polyhedron*, vol. 18. pp. 3165-3174.

FARRUGIA, L.J. 1999. WinGX suite for small-molecule single-crystal crystallography. *Journal of Applied Crystallography*, vol. 32. pp. 837-838.

FUNK, H. 1934. Über die einwirkung von niob- und tantalpentachlorid auf organische verbindungen (IV. Mitteil.). *Berichte der Deutschen Chemischen Gesellschaft*, vol. 62. pp. 1801-1808.

OTTO, S., ROODT, A., SWARTS, J.C., and ERASMUS, J.C. 1998. Electron density manipulation in rhodium(I) phosphine complexes: structure of acetylacetonatocarbonylferrocenyl diphenylphosphinerhodium(I). *Polyhedron*, vol. 17. pp. 2447-2453.

PREUSS, F., LAMMING, G., and MUELLER-BECKER, S. 1994. Oxo- und thioantantal(V)-verbindungen: Syntese von TaOX₂ und TaSX₂ (X = OR, SR), Z. *Zeitschrift für Anorganische und allgemeine Chemie*, vol. 620. pp. 1812-1820.

ROODT, A., VISSER, H.G., and BRINK, A. 2011. Structure/reactivity relationships and mechanisms from X-ray data and spectroscopic kinetic analysis. *Crystallography Reviews*, vol. 17. pp. 241-280.

SCHUTTE, M., KEMP, G., VISSER, H.G., and ROODT, A. 2011. Tuning the reactivity in classic low-spin d(6) rhenium(I) tricarbonyl radiopharmaceutical synthon by selective bidentate ligand variation (L,L'-Bid, L,L' = N,N', N,O & O,O' donor atom sets) in *fac*-[Re(CO)₃(L,L'-Bid)(MeOH)]ⁿ complexes. *Inorganic Chemistry*, vol. 50. pp. 12486-12498.

SHELDRICK, G.M. 1997. SHELXL97. Program for crystal structure refinement. University of Göttingen, Germany.

VILJOEN, J.A. 2009. Speciation and interconversion mechanism of mixed halo O,O'- and N,O-bidentate ligand complexes of hafnium. MSc dissertation, University of the Free State. 132 pp. ◆