Exploring differences in various Nb(V)- and Ta(V) tropolonato complexes by a solid-state structural comparison study

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

Synopsis

An in-depth crystallographic comparison of the crystal structures of *tetrakis*(tropolonato-κ^2O,O')niobium(V) chloride ([Nb(Trop)$_4$]Cl) and *tetrakis*(tropolonato-κ^2O,O')tantalum(V) chloride ([Ta(Trop)$_4$]Cl) was undertaken in an attempt to relate differences in complex stability previously noted in solution with solid-state characteristics such as coordination geometry, ligand bite angles and bond lengths. Significant differences of these parameters for the complexes of the two metal centres could translate to an ideal starting point for improved separation of tantalum and niobium. It was noted that the less stable Nb(V) compound, experiences a higher average degree of strain (71.39(2)°) within the bidentate chelate rings *vs.* the Ta(V) analogue (72.04(2)°). When considering the higher degree of strain, the Nb(V) complex more readily offers up one of its tropolone ligands to yield the more stable [NbO(Trop)$_3$]. The [Ta(Trop)$_4$]$^+$ cation also exhibits a more distorted square antiprismatic geometry than [Nb(Trop)$_4$]$^+$. This coordination geometry is quite distorted and could be a reason that [Ta(Trop)$_4$]$^+$ is inclined towards an energetically favourable dodecahedral geometry, contributing to a more stable conformation.

Keywords
tropolone, stability, geometry, tantalum, niobium.

Introduction

Niobium and tantalum are chemical 'twins' of the vanadium triad of the periodic table and are notoriously difficult to separate from one another and from their naturally occurring ores, due to their near-identical physical and chemical properties (Agulyansky, 2004). This similarity in behaviour has been ascribed mainly to the lanthanide contraction of the elements and also their comparable ionization energies (Hubert-Pfalzgraf, Postel and Reiss, 1987). Although the separation methods currently applied on an industrial scale, such as solvent extraction and chlorination, have been successful, these techniques remain very laborious, expensive and evolve significant chemical waste (Bose and Gupta, 2001). Accordingly, there is substantial scope for improvements in the metallurgical methods of purification of niobium and separation from tantalum.

The key to the effective and simplified separation of these elements could possibly be found in the differences in the chemical properties of two similar organic chelated moieties of these metals. Interestingly, a detailed literature review revealed a considerable shortage of knowledge in relation to the chelation behaviour of tantalum and niobium with different organic bidentate or multidentate ligands (Allen, 2002). In fact, only a single study by Muetteries and Wright (1965) revealed successful O,O'-bidentate ligand (tropolone = tropH) coordination to Ta(V) and Nb(V) metal centres using the unmodified synthons ([NbCl$_5$]$_2$/[TaCl$_5$]$_2$) in atmospheric conditions, which significantly reduces the cost of upscaling for industrial application.

In Muetteries and Wright's investigation, niobium(V) and tantalum(V) pentachlorides were reacted with acidic aqueous solutions of tropolone to form the *tetrakis*-tropolonato cations [Nb(Trop)$_4$]$^+$ and [Ta(Trop)$_4$]$^+$, with near-quantitative yields. The focus of their investigation was to determine the effect of pH and temperature on the hydrolytic stabilities of the Ta(V)- and Nb(V)- tropolonato analogues. From the preliminary ^{1}H-NMR kinetic investigation, it was found that in strongly acidic media both [Nb(Trop)$_4$]$^+$ and [Ta(Trop)$_4$]$^+$ species are stable. With increasing temperature or pH, the niobium chelate undergoes hydrolysis to the neutral [NbO(Trop)$_3$] and separates from solution. This difference in coordinative behaviour is an ideal starting point for use in a potential separation strategy.

The solution-state investigation of the formation of these compounds was quite thorough, but not much attention was given to the solid-state characteristics of the compounds (Muetteries and Wright, 1965). With this in mind, a detailed, low-temperature crystallographic investigation of the coordi-

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nation modes and intermolecular interactions could shed even more light on this nuance between Ta(V) and Nb(V) behaviour. Accordingly, the crystal structures of [Ta(Trop)$_4$]Cl and [Nb(Trop)$_4$]Cl, as obtained following the above strategy, will be discussed in this study.

Experimental

Chemicals and instruments

All chemicals used for the preparation of the compounds were of a high analytical grade and were acquired from Sigma-Aldrich (South Africa).

The ^{1}H- and ^{13}C NMR solution-state spectra were acquired on a Bruker AVANCE II 600 MHz ([1]H: 600.28 MHz; [13]C: 150.96 MHz) nuclear magnetic resonance spectrometer using an appropriate deuterated solvent (acetonitrile-d_3 [CD$_3$CN = 1.94(5) ppm]), with all chemical shifts (δ) reported in ppm. The ^{1}H NMR spectra were referenced within the sample using residual protons from the deuterated acetonitrile-d_3. The ^{13}C NMR spectra were similarly referenced internally to the solvent resonance [CD$_3$CN = 1.39(4) ppm and 118.69(8) ppm], with all reported values noted relative to tetramethylsilane (δ = 0.0 ppm).

The X-ray crystallographic data was obtained from a Bruker X8 ApexII 4K κ-CCD area detector diffractometer, specially equipped with a graphite monochromator and a MoKα fine-focus sealed tube (T = 100(2) K, λ = 0.71069 Å), which operates at 2.0 kW (40 mA, 50 kV). Preliminary unit cell predictions, as well as data collections, were done by the SMART (Bruker, 1998a) refinement program. The raw frameset data was integrated using a narrow-frame integration algorithm and reduced using Bruker SAINT-Plus and XPREP (Bruker, 1999). This reduced data was corrected for the various absorption effects using the SADABS multi-scan technique (Bruker, 1998b) and the structure solved by using direct methods on the SIR97 package (Altomare *et al.*, 1999). Final refinement was completed using the WinGX (Farrugia, 1999) software, incorporating the SHELXL (Sheldrick, 1997) package (anisotropic full-matrix least-squares refinement was done on F²). Aromatic protons were placed in geometrically idealized positions (C–H = 0.93 – 0.98 Å) and crystallographically constrained to ride on the host atoms with U$_{iso}$(H) = 1.2U$_{eq}$(C). All non-hydrogen atoms were refined with anisotropic displacement parameters. Graphics were obtained with DIAMOND (Brandenburg, 2006) (50% probability ellipsoids for non-hydrogen atoms).

Synthesis of tetrakis(tropolonato-κ²O,O')niobium(V) chloride ([Nb(Trop)$_4$]Cl) (1)

A solution of [NbCl$_5$]$_2$ (0.270 g, 1.001 mmol) in a mixture of dichloromethane (200 cm³) and ether (30 cm³) was added to a tropolone (0.489 g, 4.004 mmol) and dichloromethane (200 cm³) mixture to produce a light orange solution from which a solid precipitated. The excess solvent was removed under reduced pressure. Acetonitrile (400 cm³) was added to the residual powder and heated until dissolution was complete. Bright orange crystals separated on cooling. This compound was recrystallized from acetonitrile and vacuum-dried (120 °C, 3 hours) (0.409 g, yield 76%). IR (ATR, cm-1): υ = 723, 876, 965, 1078, 1221, 1265, 1331, 1426, 1530, 1584. ^{1}H NMR (300.13 MHz, acetonitrile-d_3, *ppm*): δ = 7.11 (d, 2H), 7.18 (t, 2H), 7.55 (t, 1H)). ^{13}C NMR (300.13 MHz, acetonitrile-d_3, *ppm*): δ = 87.8, 91.6, 101.3, 133.8.

Synthesis of tetrakis(tropolonato-κ²O,O')tantalum(V) chloride ([Ta(Trop)$_4$]Cl) (2)

A solution of [TaCl$_5$]$_2$ (0.3582 g, 1.000 mmol) in concentrated hydrochloric acid (40 cm³) and methanol (40 cm³) was added to a mixture of tropolone (0.489 g, 4.004 mmol) in concentrated hydrochloric acid (20 cm³) and methanol (320 cm³) forming a yellow precipitate. This mixed slurry was refluxed (15 minutes) until a translucent yellow solution was observed with yellow crystalline [Ta(Trop)$_4$]Cl forming on cooling. The compound was recrystallized from a hot methanol-water solution and vacuum-dried (120°C, 3 hours) (0.394 g, yield 63 %). IR (ATR, cm-1): υ = 721, 830, 1225, 1353, 1431, 1534, 1591, 1633, 3349. ^{1}H NMR (300.13 MHz, acetonitrile-d_3, *ppm*): δ = 7.18 (d, 2H), 7.32 (t, 2H), 7.87 (t, 1H)). ^{13}C NMR (300.13 MHz, acetonitrile-d_3, *ppm*): δ = 89.2, 94.3, 103.6, 127.2.

Results and discussion

A systematic comparison of the solid-state [Nb(Trop)$_4$]Cl and [Ta(Trop)$_4$]Cl structures is the main focal point of this investigation, with specific emphasis on bond angles and distances as well as the basic coordination geometry. This could give a clue as to why the coordination of tropolone is influenced so significantly by pH and temperature in solution (Muetteries and Wright, 1965) Figure 1 illustrates the crystal structures and coordination polyhedra of [Nb(Trop)$_4$]Cl (1) and [Ta(Trop)$_4$]Cl (2) and Table I compares selected crystallographic parameters of the compounds.
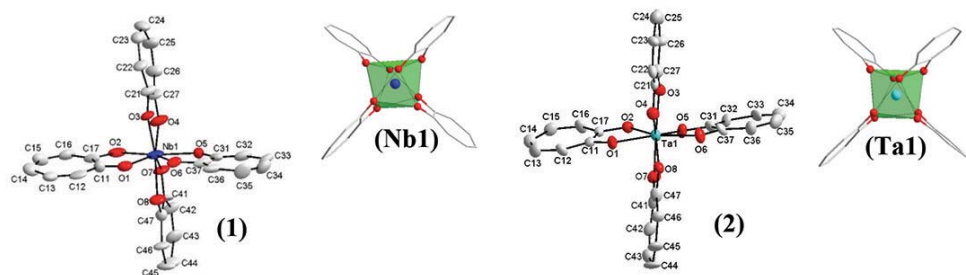

Figure 1—Illustration of the structures and coordination polyhedron of [Nb(Trop)$_4$]$^+$ (1) and [Ta(Trop)$_4$]$^+$ (2) showing general numbering scheme. (Note that for (2) an observed coordination configuration for Ta2 (omitted for clarity) was nearly identical with that illustrated for Ta1). Atomic displacement ellipsoids are drawn at 50% probability displacement level. Hydrogen atoms, counter-ion and Ta2 were omitted for clarity

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Table I

Crystallographic and refinement detail of compounds discussed in this investigation

Crystal formula	[Nb(Trop)$_4$]Cl (1)	[Ta(Trop$_4$)]Cl (2)
Empirical formula	C$_{28}$H$_{20}$NbO$_8$	C$_{28}$H$_{20}$O$_8$Ta
Formula weight (g.mol^{-1})	537.80	625.55
Crystal system, space group	Triclinic, P$\bar{1}$	Monoclinic, C2/c
a, b, c (Å)	10.027(3), 12.907(3), 14.750(4)	19.626(3), 20.360(3) 22.446(3)
α, β, γ (°)	68.776(4), 78.141(3), 81.860(4)	90, 96.050(3), 90
Volume (Å^3), Z	1778.3(1), 2	2919.3(4), 4
Density (calculated, Mg/m^3)	1.371	1.506
Crystal colour, crystal size (mm^3)	Orange, 0.53 × 0.13 × 0.09	Yellow, 0.25 × 0.18 × 0.10
Absorption coefficient μ (mm^{-1})	0.399	3.802
F(000), theta range	583, 2.45–27.70°	3828, 1.35–28.00°
Reflections collected, independent reflections, R$_{int}$	6119, 3518, 0.1556	4792, 6477, 0.1617
Completeness to 2θ (°, %)	28.00, 97.6	28.00, 100
Data, restraints, parameters	20299, 0, 370	10753, 0, 240
Goodness-of-fit on F^2	1.106	1.152
Final R indices [I>2sigma(I)]	R$_1$ = 0.1995 wR$_2$ = 0.2956	R$_1$ = 0.1131 wR$_2$ = 0.3584
R indices (all data)	R$_1$ = 0.2586 wR$_2$ = 0.3470	R$_1$ = 0.1803 wR$_2$ = 0.4097
Largest diff. peak and hole (e.Å^{-3})	0.40, −1.04	3.31, −2.15

The Nb(V) (1) compound crystallizes in the triclinic space group, P1̄, with one independent molecule in the asymmetric unit. For this molecule, a Nb(V) metal centre is coordinated to four independent tropolonato ligands arranged in a distorted D_2-square antiprismatic geometry. This type of arrangement is extremely rare and has hardly ever been observed for 8-coordinated Nb(V) complexes (Booyens and Oglvie, 2008.

The Ta(V) (2) compound crystallizes in the monoclinic space group, $C2/c$, with one full [Ta(Trop)$_4$]$^+$ cation (**Ta1**) and half of another [Ta(Trop)$_4$]$^+$ (**Ta2**) moiety in the asymmetric unit. In the case of **Ta1**, a metal centre is surrounded by four independent tropolonato ligands arranged in a distorted D_2-square antiprismatic geometry. In contrast, for **Ta2**, the Ta2 atom is located on a special position and is coordinated to two tropolonato ligands with the other half of the cation being generated through the mirror plane. **Ta2** also illustrates a distorted D_2-square antiprismatic coordination geometry. In spite of the two different crystallization modes of the two independent Ta(V) complexes, the average bite angles stay comparable with each other and typically 1° greater than for the Nb(V) complex. This type of arrangement has never been noted for a Ta(V) structure and only on one occasion in the structure of *tetrakis*(oxalato)tantalum(IV) for the Ta(IV) species (Cotton, Diebold and Roth, 1987).

A large residual electron density of 3.31 was located at a distance of 3.48 Å from C14 for compound 2 (see Table I). Although this value is very significant, it is isolated from the coordination sphere and need not be assigned for this investigation as it has minimal effect with relation coordination geometry around the metal centre.

When comparing the various bond distances and angles listed in Tables II and III, several trends are noticed. These tendencies are now discussed and compared systematically.

Nb-O and Ta-O bond distances

As expected, the average Nb-O (2.083(1) Å) and Ta-O (2.092(1) Å) bond distances correlate very well with each other. Similar average metal-oxido distances have been noted on several occasions in past studies (Allen, 2002; Davies and Jones, 2005; Peric, Brnicevic and Juric, 2009; Calderazzo and Englert, 1998; Roodt, Otto and Steyl, 2003; Schutte, Roodt and Visser, 2012). This phenomenon can probably be attributed to the near-identical covalent radii of both Ta and Nb. Although not much in relation to separation studies can be derived from this, it indicates that the assumption made – that the inferior crystal quality would not significantly influence coordinative crystal data – is acceptable.

O-metal-O bond angles and O⋯O bite distances

Interestingly, a substantial difference (max. 1.38°) in bidentate bite angle is noted between 1 and. 2. From this it can be concluded that the chelate ring of the Nb(V) compound is significantly more strained. This could also give a clue as to why a decrease in pH has a different effect on each metal. As the pH of the solution increases, conditions become less advantageous for *tetrakis*-coordination, preferring the more stable *tris*-coordinated oxido species (if an oxygen-donating substance is available). The smaller steric demand of the four tropolone ligands in the Nb(V) case will promote nucleophilic attack by OH$^-$ to the metal centre. Due to the fact that the chelate ring in the Nb(V) compound is more strained it could more readily sacrifice one of its tropolone ligands for increased stability.

Bite distances are fairly well correlated to ligand bite angle and, as expected, the average distances for 2 (2.447(1) Å) and 1 (2.431(1) Å) differ quite significantly.

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Table II

Selected bond lengths and bite distances for [Nb(Trop)$_4$]Cl and [Ta(Trop)$_4$]Cl

[Nb(Trop)$_4$Cl]		[Ta(Trop)$_4$Cl] (Ta1)		[Ta(Trop)$_4$Cl] (Ta2)	
Atoms	Bond length (Å)	Atoms	Bond length (Å)	Atoms	Bond length (Å)
Nb1-O1	2.094(1)	Ta1-O1	2.098(1)	Ta2-O9	2.087(1)
Nb1-O2	2.099(1)	Ta1-O2	2.068(1)	Ta2-O10	2.095(1)
Nb1-O3	2.092(1)	Ta1-O3	2.098(1)	Ta2-O11	2.076(1)
Nb1-O4	2.087(1)	Ta1-O4	2.093(1)	Ta2-O12	2.073(1)
Nb1-O5	2.021(1)	Ta1-O5	2.088(1)		
Nb1-O6	2.096(1)	Ta1-O6	2.091(1)		
Nb1-O7	2.085(1)	Ta1-O7	2.063(1)		
Nb1-O8	2.089(1)	Ta1-O8	2.134(1)		
O1···O2	2.454(1)	O1···O2	2.459(1)	O9···O10	2.431(1)
O3···O4	2.426(1)	O3···O4	2.456(1)	O11···O12	2.445(1)
O5···O6	2.401(1)	O5···O6	2.439(1)		
O7···O8	2.442(1)	O7···O8	2.452(1)		

Table III

Selected bond and plane angles for [Nb(Trop)$_4$]Cl and [Nb(Trop)$_4$]Cl

[Nb(Trop)4C1]		[Ta(Trop)$_4$Cl] (Ta1)		[Ta(Trop)$_4$Cl] (Ta2)	
Atoms	Angle (°)	Atoms	Angle (°)	Atoms	Angle (°)
O1-Nb1-O2	71.34(1)	O1-Ta1-O2	72.34(2)	O9-Ta2-O10	71.09(2)
O3-Nb1-O4	70.96(2)	O3-Ta1-O4	71.74(1)	O11-Ta2-O12	72.22(1)
O5-Nb1-O6	71.63(1)	O5-Ta1-O6	72.40(2)		
O7-Nb1-O8	71.60(2)	O7-Ta1-O8	71.69(1)		
Out-of-plane distortion (O1-O2-O3-O4)	28.46(3)	Out-of-plane distortion (O1-O2-O3-O4)	31.01(1)	Out-of-plane distortion (O9-O10-O11-O12)	26.99(2)
Out-of-plane distortion (O5-O6-O7-O8)	27.47(2)	Out-of-plane distortion (O5-O6-O7-O8)	27.61(2)		
Trop1/Trop3	174.34(2)	Trop1/Trop3	171.54(1)	Trop5/Trop5'	167.06(1)
Trop2/Trop4	174.71(3)	Trop2/Trop4	169.05(1)	Trop6/Trop6'	173.81(1)

Coordination geometry

Table III highlights the fact that the degree of distortion from D_2-square antiprismatic (D_2-SAP) geometry towards dodecahedral geometry is much more pronounced for **2**. For ideal SAP geometry the ligand planes would have to lie opposite each other at an ideal 180° angle. When considering the 'ligand planes' as described in Table III, it is obvious that the distortion from ideal 180° is much more pronounced in the case of the **2** compound, although a significant distortion is also noted for **1**. Figure 2 further illustrates this distortion by illustrating the outward bends of the various OA-OB-OC-OD planes for both complexes. Again, this is independent of the two different crystallization modes of **Ta1** and **Ta2**.

Some correlation can be drawn between the observations by Muetteries and Wright in solution and this distortion noted in solid state (Muetteries and Wright, (1965). From basic crystallography it is known that dodecahedral geometry is an energetically favourable coordination mode, affording a more stable compound. It might then seem that the robustness of **2** *vs.* **1** in solution could also be ascribed to the more energetically favourable coordination mode (Hutchings *et al.*, 2014). Accordingly, an argument can be proposed that the 2 has dodecahedral geometry and is significantly distorted towards the D_2-SAP geometry. Although this notion is not irrefutably conclusive, it cannot be ignored.

Conclusions

Some interesting observations were made from the comparison of the [Ta(Trop)$_4$]Cl and [Nb(Trop)$_4$]Cl solid-state crystal structures. The bite angles of both compounds revealed that the [Nb(Trop)$_4$]Cl compound experiences a higher degree of strain within the chelate ring but less steric repulsion, thus is more prone to nucleophilic attack. This could have interesting implications for complex stability. When considering the higher degree of strain (less energetically favourable) within the Nb(V) chelate ring, this complex could more readily sacrifice one of its tropolone ligands for the sake of obtaining the more stable [NbO(Trop)$_3$] complex (average bite angle 71.39(2)°).

Secondly, the [Ta(Trop)$_4$]$^+$ cation exhibits a more distorted square antiprismatic geometry compared with [Nb(Trop)$_4$]$^+$. In fact, the coordination geometry is so distorted that [Ta(Trop)$_4$]$^+$ might favour the more energetically favourable dodecahedral geometry. This might further contribute to the Ta(V) complex stability.

These observations from this crystallographic study of Nb(V) and Ta(V) tropolonates substantiate the results noted from the solution-state investigation (Muetteries and Wright, 1965). With this enhanced knowledge of the intricacies of these systems, it is possible to investigate separation methods such as separation by ionic resins (in solution:

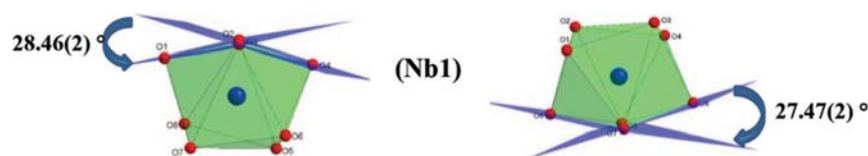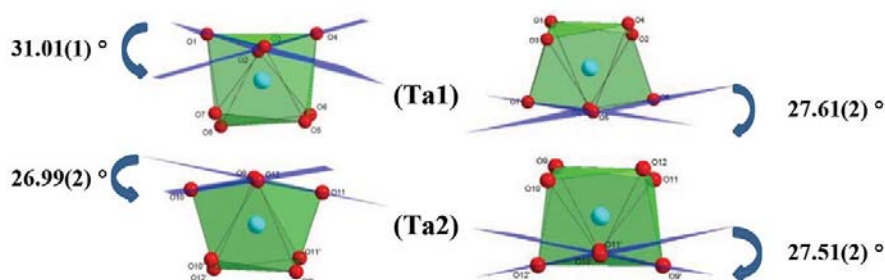# Exploring differences in various Nb(V)- and Ta(V) tropolonato complexes

Figure 2—Illustration of the distortion of the SAP coordination polyhedron found in 1. (Left) Outward bend of the top-most atoms; 28.46(2)° (right) 27.47(2)° for bottom plane

Ta1: Outward bend of the top-most plane of 31.01(1)° and 27.61(2)° for the bottom plane
Ta2: Outward bend of the top-most plane of 26.99(2)° and 27.51(2)° for the bottom plane

Figure 3—Illustration of the distortion of the SAP coordination polyhedron found in 2

neutral $[NbO(Trop)_3]$ vs. cationic $[Ta(Trop)_4]^+$ at slightly acidic pH values), sublimation (differences in solid-state stability should cause differences of the sublimation temperatures of these Nb(V) and Ta(V) analogues) as well as fractional crystallization, which could be upscaled for industrial use.

Although comparison of reaction properties in solution with solid-state crystal structures should be done with care, this solid-state investigation has already shed some more light as to why the properties of the Nb(V) and Ta(V) compounds differ significantly.

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