Synthesis of $Nb(O_2H_5C_7)_3Y$ (Y = O, S and Se): Crystal Structure of Oxo-tris-(tropolonato)niobium(V) Monohydrate: a Seven Coordinate Monomer Containing a Terminal Nb=O Bond

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Abstract

The crystal structure of NbT_3O ($T = O_2H_5C_7$) has been determined. Crystals are monoclinic; space group $P2_1/c$ with $a = 7.328(7)$, $b = 16.669(13)$, $c = 16.373(13)$ Å; $\beta = 99.5(1)°$ and $Z = 4$. 3382 reflections were collected on a diffractometer of which 1257 were used in the final refinement; the structure being refined to $R_w = 0.087$. The crystal contains discrete molecules of NbT_3O in which the metal atom is seven coordinate having a distorted pentagonal-bipyramid configuration. The terminal oxygen atom occupies an axial position (1.712(14) Å). The Nb–O(trop) bond lengths range from 2.070(15) to 2.197(14) Å. The analogous compounds NbT_3S, and NbT_3Se have been obtained by reaction of NbT_3O with $[(Me_3Si)_2Y]$ (Y = S or Se). These latter species are believed to contain terminal Nb=Y bonds with the metal in a similar seven coordinate environment to that found for the oxo compound.

Introduction

There are few niobium(V) species that are stable and soluble in aqueous media. One of the few such species is $[NbT_4]^+$ which is formed when niobium(V) chloride is treated with tropolone in acidic conditions [1]. However in solutions with pH > 3, or the temperature above 60 °C, it undergoes hydrolysis and NbT_3O is formed [1]. The metal atom in $[NbT_4]^+$ has been shown to be eight coordinate with the oxygen atoms forming an irregular bicapped trigonal prism that is distorted towards a dodecahedron [2] but the structure of NbT_3O is unknown although it has been suggested that it may contain Nb–O–Nb bridging bonds [1] like those in $NbOCl_3$ [3] as the compound is relatively insoluble in water and its infra-red spectrum was reported to be very different to that of VT_3O [1]. We have synthesised a number of compounds with Nb=Y or Nb–Y–Nb bonds (Y = O, S, Se) [4] and as part of this continuing programme have studied the structure of NbT_3O and attempted to make its sulphur and selenium analogues *i.e.* NbT_3Y (Y = S or Se).

Experimental

Tropolone (Aldrich) was recrystallised from n-hexane, while MeCN (B.D.H.) was dried with P_4O_{10} and then vacuum distilled on an all-glass vacuum line onto Lind 4 Å molecular sieves. $(Me_3Si)_2S$ (Fluka), Me_3SiCl (Aldrich) and 'Super Hydride' ($LiEt_3BH$ in tetrahydrofuran, Aldrich) were used as supplied.

Preparation of $(Me_3Si)_2Se$

Caution: this reaction should be carried out in an efficient fume cupboard.

Dry selenium shot (1.97 g, 25 mmol) was placed in a dry 250 cm^3 round-bottomed flask which was flushed with nitrogen and cooled to 0 °C. To the flask was added, over a 15 min period, 50 cm^3 of 1 M triethylborohydride in tetrahydrofuran (50 mmol 'Super Hydride'). The contents were allowed to warm to room temperature and stirred for 1 h during which time a white suspension was formed. The resulting mixture was cooled to 0 °C and Me_3SiCl (7.0 cm^3, 55 mmol) added via a syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The solvent, and any excess of Me_3SiCl, were removed by distillation at reduced pressure (50 °C, 10 torr). When all the solvent had been removed the temperature was raised, the pressure lowered (72 °C, 2.5 torr) and the product distilled. The product, $(Me_3Si)_2Se$, was a colourless, air-sensitive liquid which was distilled into a storage ampoule fitted with a Rotaflow tap and septum cap. The purity of the product was confirmed by measurement of its ^1H NMR spectrum in $CDCl_3$ ($\delta = 0.50$ ppm [5]).

Preparation of NbT_3O

Oxo-tri(tropolonato)niobium(V) was prepared from niobium(V) chloride and tropolone as previously described [1]. Samples for analysis were

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dried at 100 °C for 24 h. *Anal.* Found: Nb, 19.6; C, 52.7; H, 3.3. Calc. for $NbC_{21}H_{15}O_7$: Nb, 19.7; C, 53.4; H, 3.2%.

Preparation of NbT_3Y ($Y = S$ or Se)

Oxo-tris(tropolonato)niobium(V) (2.0 g) was placed in a dry round-bottomed flask containing a magnetic follower. Under a flow of dry nitrogen $(Me_3Si)_2Y$ (Y = S or Se) (5 cm^3 a five-fold excess) was syringed into the flask. The flasked was cooled in liquid nitrogen and evacuated. Dry MeCN (25 cm^3) was distilled into the flask under reduced pressure. The mixture was allowed to warm to room temperature and stirred at that temperature for 3 d. The product, which was insoluble, was isolated by vacuum-line filtration and washed with fresh quantities of MeCN. The material was pumped for 48 h and stored either *in vacuo* or under dry nitrogen. The yield was approximately 65%. *Anal.* Calc. for $NbC_{21}H_{15}O_6S$: Nb, 19.0; C, 51.6; H, 3.1%. Found: Nb, 18.9; C, 50.8; H, 2.8%. Colour orange. Calc. for $NbC_{21}H_{15}O_6Se$: Nb, 17.4; C, 47.1; H, 2.8. Found: Nb, 17.5; C, 47.9; H, 2.7%. Colour dark brown.

Crystal Structure Determination

Yellow crystalline plates of $NbT_3O{\cdot}H_2O$ were obtained by allowing a hot solution of NbT_3O in pyridine to cool slowly.

Crystal data

$NbT_3O{\cdot}H_2O$, $NbO_8C_{21}H_{17}$, $M = 490.0$, monoclinic, $a = 7.328(7)$, $b = 16.669(13)$, $c = 16.373(13)$ Å, $\beta = 99.5(1)°$, $U = 1972.6$ Å^3, $D_m = 1.60(3)$ g cm^{-3}, $D_c = 1.63$ g cm^{-3}, $Z = 4$, $F(000) = 992$, Mo Kα radiation, $\lambda = 0.7107$ Å, $\mu = 9.59$ cm^{-1}. Space group $P2_1/c$.

A crystal of approximate size 0.50 × 0.33 × 0.15 mm was mounted on a Stoe Stadi-2 Diffractometer and data collected via variable width ω scan. Background counts were 20 s and the scan rate of 0.033° s^{-1} was applied to a width of $(1.5 + \sin \mu/\tan \theta)$. 3382 Independent reflections with $2\theta < 50°$ of which 1257 with $I > 3\sigma(I)$ were used in the final refinement. An empirical absorption correction was applied. The structure was determined by the usual heavy atom method. The water molecule was located in two positions which were given occupancy factors of 0.75 and 0.25. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms, bound to carbon, were fixed in trigonal positions while the hydrogen atoms bound to oxygen were not located. The structure was refined by full-matrix least squares to R 0.085 (R_w 0.087). The weighting scheme used was $w = 1/[\sigma^2(F) + 0.003F^2]$. All calculations were carried out with SHELX76 [6] and our own programs on the University of Reading Amdahl V7 computer. Atomic co-ordinates are given in Table I and the molecular dimensions of the coordination sphere in Table II.

TABLE I. Atomic Coordinates ($\times 10^4$) for 1 with Estimated Standard Deviations in Parentheses

Atom	x	y	z
Nb	1999(3)	2269(1)	3173(1)
O(1)	−329(19)	2188(10)	3175(9)
O(2)	2342(23)	1361(10)	2334(9)
O(3)	2637(20)	1126(9)	3823(9)
O(4)	2508(22)	2545(8)	4454(8)
O(5)	4986(20)	2409(10)	3597(8)
O(6)	2091(25)	3579(9)	3254(10)
O(7)	1923(23)	2751(11)	2003(9)
O(8A)	1464(31)	4535(15)	4753(13)
O(8B)	5000(0)	5000(0)	5000(0)
C(1)	2604(29)	613(16)	2514(15)
C(2)	2615(37)	45(19)	1937(14)
C(3)	2872(42)	−791(18)	1981(16)
C(4)	3115(34)	−1259(15)	2662(17)
C(5)	3353(38)	−1014(15)	3470(19)
C(6)	3221(36)	−275(17)	3785(18)
C(7)	2835(30)	476(13)	3413(14)
C(8)	4136(29)	2743(15)	4839(13)
C(9)	4446(35)	2971(12)	5679(14)
C(10)	5963(35)	3159(12)	6213(15)
C(11)	7764(34)	3137(14)	6111(16)
C(12)	8437(28)	2914(16)	5400(15)
C(13)	7542(31)	2675(16)	4625(15)
C(14)	5674(35)	2596(14)	4359(14)
C(15)	1954(33)	3991(14)	2619(16)
C(16)	2053(32)	4816(13)	2639(15)
C(17)	1992(33)	5377(16)	2028(18)
C(18)	1842(31)	5305(15)	1207(20)
C(19)	1651(32)	4597(15)	751(16)
C(20)	1721(31)	3797(18)	1038(14)
C(21)	1937(35)	3536(16)	1871(14)

Results and Discussion

The compound NbT_3O is readily prepared from $NbCl_5$ and tropolone [1]. However the analogous sulphur and selenium compounds NbT_3Y (Y = S or Se) have not been reported. We have successfully prepared these later species by allowing NbT_3O to react with $(Me_3Si)_2Y$ (Y = S or Se) in MeCN [7]. The three compounds NbT_3O, NbT_3S, and NbT_3Se are yellow, orange and dark brown respectively reflecting the lowering of the energy required for the $Nb \leftarrow Y$ (Y = O, S, or Se) charge-transfer transition on substituting oxygen first by sulphur and then selenium.

The infra-red spectra for all three compounds are very similar; the only variation being in the bands that can be ascribed to ν(Nb=O), ν(Nb=S), and ν(Nb=Se). In the oxo compound ν(Nb=O) is assign-

TABLE II. Molecular Dimensions in the Coordination Sphere. Distances (A) Angles (°)

Nb–O(1)	1.712(14)
Nb–O(2)	2.086(15)
Nb–O(3)	2.194(15)
Nb–O(4)	2.119(13)
Nb–O(5)	2.197(14)
Nb–O(6)	2.189(15)
Nb–O(7)	2.070(15)
O(1)–Nb–O(2)	99.9(6)
O(1)–Nb–O(3)	93.6(6)
O(2)–Nb–O(3)	69.6(5)
O(1)–Nb–O(4)	91.6(6)
O(2)–Nb–O(4)	142.0(6)
O(3)–Nb–O(4)	73.7(5)
O(1)–Nb–O(5)	161.7(5)
O(2)–Nb–O(5)	93.6(6)
O(3)–Nb–O(5)	79.5(5)
O(4)–Nb–O(5)	70.2(5)
O(1)–Nb–O(6)	95.7(7)
O(2)–Nb–O(6)	139.3(6)
O(3)–Nb–O(6)	146.6(6)
O(4)–Nb–O(6)	74.0(5)
O(5)–Nb–O(6)	81.7(6)
O(1)–Nb–O(7)	99.1(6)
O(2)–Nb–O(7)	70.1(6)
O(3)–Nb–O(7)	139.2(6)
O(4)–Nb–O(7)	143.6(6)
O(5)–Nb–O(7)	97.1(6)
O(6)–Nb–O(7)	70.4(6)

ed to a band at 914 cm^{-1} which is in agreement with the assignment given in the seven coordinate species Nb(S$_2$CNEt$_2$)$_3$O (900 cm^{-1}) [8]. The occurrence of such a band in NbT$_3$O suggested that the compound did not contain Nb–O–Nb chains as previously postulated [1] and the suggestion was subsequently confirmed by the single crystal X-ray analysis which is discussed later. The ν(Nb=S) and ν(Nb=Se) vibrations are assigned to bands at 494 and 350 cm^{-1}, respectively. The value observed for ν(Nb=S) is in accord with that reported for the seven coordinate Nb(S$_2$CNEt$_2$)$_3$S (498 cm^{-1}) [4] and slightly lower than the values found for a number of six coordinate compounds (540 to 515 cm^{-1}) [9]. There are few reports of ν(Nb=Se) assignments. However, absorptions at 371 cm^{-1} and 334 cm^{-1} in the spectra of NbSeCl$_3$ and NbSeBr$_3$ respectively have been assigned to ν(Nb=Se) [10].

For the tungsten compounds WYCl$_4$ (Y = O, S, Se) it was found that the approximate force constants for ν(W=Y) were 9.2, 5.0 and 4.9 aJ Å^{-2} for Y = O, Y = S and Y = Se, respectively. Calculations for ν(Nb=Y) for NbT$_3$Y give values of 6.7, 3.4 and 3.1 aJ Å^{-2} for Y = O, Y = S and Y = Se, respectively. The trend in the values is the same for tungsten and niobium and reveals that there is a major reduction in bond order on going from M = O to M = S (M = Nb or W) reflecting a decrease in p$_\pi$ to d$_\pi$ donation. The difference between the niobium values and the tungsten values for a given chalcogen reflects the difference in coordination number but more especially a difference in oxidation number of the metal.

Crystal Structure Determination of NbT$_3$O

The structure, which is shown in Fig. 1 together with the atomic numbering scheme, consists of discrete NbT$_3$O units (molecular dimensions of the coodination sphere are given in Table II). The niobium atom is seven coordinate being bonded to seven oxygen atoms that form a distorted pentagonal bipy-

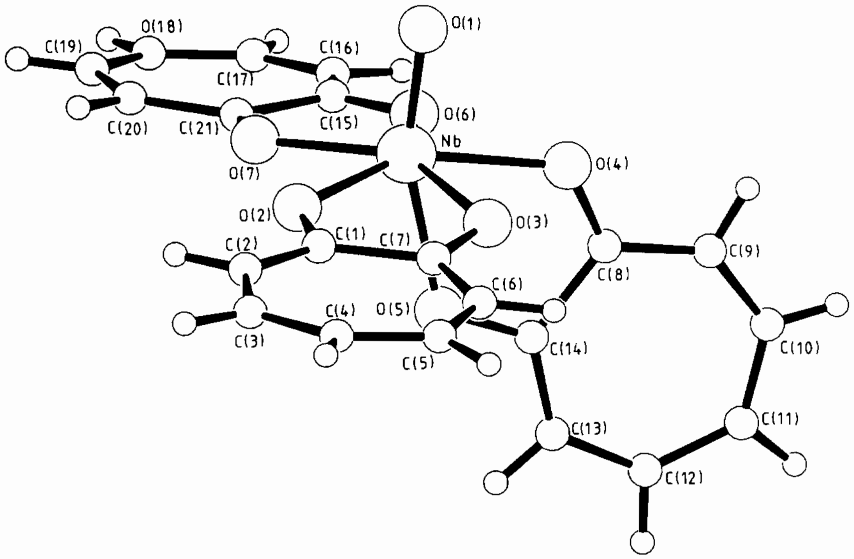

Fig. 1. Oxo-tris(tropolonato)niobium(V).

ramid. The terminal oxygen atom occupies the axial site, two chelating tropolone ligands are in the equatorial plane while the remaining equatorial and axial positions of the trigonal bipyramid are filled by the oxygen atoms of the unique tropolone ligand. This arrangement is by far the most frequently found conformation for seven-coordinate molecules of the general formula M(bidentate)$_3$(monodentate) [11, 12]. The Nb–O terminal bond (1.712(14) Å) is of similar length to those found in Nb(S_2CNEt_2)$_3$O (1.74 Å [13]), $[Nb\{C_2O_4\}_3O]^{3-}$ (1.71 Å [14]) and $[Nb\{C_2O_4\}_2\{H_2O\}_2O]^-$ (1.69 Å [15]). Comparable distances are also found in a number of niobium oxohalide adducts (1.66 to 1.71 Å [13, 16–21]).

The Nb–O(tropolone) distances range from 2.070(15) to 2.197(14) Å, the variations reflecting the positions of the atoms in the coordination sphere. The structure is distorted from the ideal pentagonal bipyramid; using our method of polyhedron fitting [11] we calculate that the present structure has a r.m.s. deviation of 0.13 Å from that of an ideal pentagonal bipyramid. The deviations are due to the exigencies of the multiple bond and the constraints of the three chelate rings. Such deviations are common to the vast majority of M(bidentate)$_3$(monodentate) compounds in this geometry. Thus the niobium atom is moved towards the terminal oxygen atom by 0.22 Å out of the plane of the five equatorial oxygen atoms (maximum displacement 0.03 Å). The *trans* influence of this multiple bond lengthens the other axial bond, Nb–O(5) to 2.197(14) Å. It is interesting that in the equatorial plane the two bonds furthest from the unique ligand, *viz.* Nb–O(2) and Nb–O(7) are considerably shorter at 2.086(19), 2.070(15) Å than Nb–O(3) 2.194(15) and Nb–O(6) 2.189(15) Å. This probably reflects steric crowding in the equatorial plane caused by the unique ligand. It would seem that these shorter distances represent unstrained Nb–O bonds particularly as in the eight-coordinate $[NbT_4]^+$, the mean Nb–O distance is 2.088(5) Å [2].

It is significant that O(4) is coplanar with the other four oxygen atoms in the equatorial girdle. This means that the distortion involved in fitting the tropolone ligand (bite angle *ca.* 70°) into the ideal 90° degree angle (subtended by an axial and an equatorial site) is achieved by shifting the position of the axial atom, O(5), rather than the equatorial atom O(4). Indeed O(5) moves out of the axial position by *ca.* 20° so that the O(1)–Nb–O(5) angle is 161.7(5)° instead of the ideal 180°.

The chelating tropolone ligands are relatively planar; with no significant angle of intersection between the NbO_2C_2 and C_7 rings. For all three tropolone ligands no contributing atom deviates from the plane by more than 0.10 Å.

The water molecules interact with each other, (O(8A)···O(8B) $[-x, 1-y, 1-z]$ 2.87(3) Å; O(8A)···O(8B) $[-1+x, y, z]$ 2.67(3) Å), rather than with the NbT_3O molecules. There are no intermolecular distances less than the sum of van der Waals' radii.

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