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Formation of a novel μ_3-borate-capped triniobium cluster *via* hydrolysis of a hydridotris(pyrazol-1-yl)borate ligand

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The novel μ_3-hydroxotrioxoborato-capped cluster $[Nb_3\{\mu_3\text{-}BO_3(OH)\}(\mu\text{-}O)_3\{HB(pz)_3\}_3]$ **1** has been obtained following evaporation to dryness of aqueous HCl solutions of $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ and treatment with ethanolic potassium hydridotris(pyrazol-1-yl)borate, K[HB(pz)$_3$]. The capping borate group derives from hydrolysis of a $HB(pz)_3^-$ ligand in the presence of the aqua precursor. Air oxidation of **1** results in complete fragmentation, loss of the borate cap and reassembly in the form of a rectangular tetranuclear oxo-bridged product.

The green air-sensitive solutions that result following treatment of the trivalent niobium complex [NbCl$_3$(dme)] with aqueous mineral acids have been shown to contain triangular μ-oxo-bridged clusters.[1,2] Similar green solutions have also been reported to result from zinc reduction of NbCl$_5$ in HCl–ethanol mixtures.[3] A combination of redox titrations and oxygen-17 labelling NMR studies following cation-exchange column purification together with more recent investigations by niobium K-edge EXAFS[4] provides support for the green solutions obtained from aqueous HCl as containing the μ_3-chloro-capped aqua species $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$. Earlier work by Cotton *et al.*[2] showed that the corresponding μ_3-sulfido capped cluster $[NH_4]_3[NMe_4]_3[Nb_3(\mu_3\text{-}S)(\mu\text{-}O)_3(NCS)_9]$ can be isolated following treatment of similar green niobium solutions with ethanolic NCS$^-$. The capping sulfur atom here is believed to derive from decomposition of NCS$^-$ giving some S^{2-} which is then captured by the cluster. This observation points to a degree of lability at the capping μ_3-chloro group.[1]

In seeking to expand further the chemistry of lower-valent species of niobium (and tantalum) we have found that the green HCl solutions can be evaporated to dryness giving a chloride salt, assumed to be $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_{9-x}Cl_x]Cl_{4-x}$ ($x = 0$–4), which is soluble in primary alcoholic solvents. In previous work[1] we reported evidence of a red-brown niobium complex which can be isolated following dissolution of the above salt in ethanol and treatment with ethanolic potassium hydridotris(pyrazol-1-yl)borate, K[HB(pz)$_3$]. X-Ray-quality single crystals of this complex, obtained following crystallisation from CHCl$_3$ or CH$_2$Cl$_2$ solutions, have now been shown to contain the novel μ_3-hydroxotrioxoborate-capped mixed-valence triangular cluster $[Nb_3\{\mu_3\text{-}BO_3(OH)\}(\mu\text{-}O)_3\{HB(pz)_3\}_3]$ **1**. We report herein the crystal structure of this complex together with the structural characterisation of an unusual tetranuclear oxo-bridged niobium(V) oxidation product **2**. The reactions leading to the formation of **1** and **2** successively from $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_{9-x}Cl_x]^{(4-x)+}$ are discussed.

Experimental

Preparations

$[Nb_3\{\mu_3\text{-}BO_3(OH)\}(\mu\text{-}O)_3\{HB(pz)_3\}_3]$ 1. The synthetic route to complex **1** from the chloride salt of $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_{9-x}Cl_x]^{(4-x)+}$ in ethanol together with elemental analysis, FAB mass and ^{1}H and ^{13}C NMR spectral data on its ethanol (methanol)–water solvate were reported earlier.[1] X-Ray-quality crystals (red blocks) were obtained by diffusion of diethyl ether into a solution of **1** in CH$_2$Cl$_2$. The loosely bound solvent molecules are lost during collection of the X-ray data. The crystals are diamagnetic and non-conducting.

$[\{NbO(\mu\text{-}O)[HB(pz)_3]\}_4]$ 2. The red blocks of complex **1** are perfectly air stable. However yellow-green blocks of **2** were eventually isolated from slowly air evaporated solutions of **1** in CH$_2$Cl$_2$–diethyl ether (1 : 1) over several hours. These were separated, washed with diethyl ether and dried in a desiccator over silica gel (yield ≈80% based on **1**). Crystals of **2** were sometimes observed cocrystallising alongside those of **1**. The FAB mass, microanalytical, infrared and NMR data showed them to consist of the tetranuclear oxo-bridged oxoniobium(V) complex $[\{NbO(\mu\text{-}O)[HB(pz)_3]\}_4]$, M_r 1350.9 (Found: C, 32.35; H, 3.12; N, 25.18. Calc. for $C_{36}H_{40}B_4N_{24}Nb_4O_8$: C, 31.98; H, 2.96; N, 24.87%); positive-ion FAB mass spectrum *m*/*z* 1352 (M^+); infrared (KBr disc) 917 cm^{-1} (Nb=O); δ_H(CDCl$_3$) 7.27 (1 H, s, CHCl$_3$), 6.21 (9 H, m), 7.72 (9 H, m) and 8.43 (9 H, m) (pyrazolyl); δ_C(CD$_2$Cl$_2$) 54.2 (1 C, t, CD$_2$Cl$_2$–CH$_2$Cl$_2$), 106.6 (1 C, s), 137.0 (1 C, s) and 146.9 (1 C, s) (pyrazolyl). The crystals are diamagnetic and non-conducting.

X-Ray crystallography

X-Ray data for complexes **1** and **2** were collected at 20 ± 1 °C on a Rigaku AFC7S diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å). The structure was solved using direct methods[5] and expanded using Fourier techniques.[6] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Neutral atom scattering factors were taken from Cromer and Waber.[7] Anomalous dispersion effects were included in F_c.[8] Lorentz-polarisation corrections were applied. All calculations were performed using the TEXSAN[9] crystallographic software package. Crystal data, along with the structure solution and refinement parameters for both **1** and **2** are listed in Table 1.

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Results and Discussion

Complex **1** has a crystallographic three-fold axis of symmetry relating the Nb atoms. A view of **1** looking down the three-fold axis is shown in Fig. 1. Selected bond lengths and angles are given in Table 2. The three edges of the triangle are doubly bridged by six oxygen atoms, three belonging to bridging oxygens of a puckered Nb$_3$O$_3$ ring and three as part of the capping hydroxotrioxoborate ligand. The core structure around the Nb$_3$ triangle is shown more clearly in the simplified side view, Fig. 2, in which the $HB(pz)_3^-$ ligands have been omitted for

Table 1 Summary of data collection, solution structure and refinement for compounds **1** and **2***

	1	**2**
Empirical formula	$C_{27}H_{31}B_4N_{18}Nb_3O_7$	$C_{18}H_{20}B_2N_{12}Nb_2O_4$
M	1041.62	675.43
Crystal colour, habit	Red, block	Yellow-green, block
Crystal dimensions/mm	0.15 × 0.15 × 0.10	0.50 × 0.20 × 0.20
Crystal system	Trigonal	Tetragonal
Space group	*R*3 [no. 146 (hexagonal axes)]	*P*4/*ncc* (no. 130)
No. reflections used for unit-cell determination (2θ range/°)	25 (19.5–23.3)	11 (7.1–9.6)
a/Å	18.178(4)	16.321(6)
c/Å	10.553(5)	23.685(8)
U/Å^3	3020(1)	6308(4)
Z	3	8
D_c/Mg m^{-3}	1.718	1.419
F(000)	1554.00	2672.00
μ(Mo-Kα)/cm^{-1}	9.07	7.68
$2\theta_{max}$/°	49.9	50
No. reflections measured		
Total	2609	1951
Unique	1169 ($R = 0.026$)	1951
Observed	1043	1344
No. observations [$I > 3.00\sigma(I)$]	1043	1344
No. variables	177	173
Reflection/parameter ratio	14.03	7.77
R, *R′*	0.030, 0.037	0.049, 0.061
Goodness of fit	2.19	2.54
Maximum shift/error in final cycle	0.02	0.03
Maximum, minimum peak in final difference map/e Å^{-3}	0.91, −0.40	1.24, −0.64

* Details in common: ω–2θ scans: scan rate 16° min^{-1} (in ω), up to four scans: scan width (1.10 + 0.35 tan θ)°; full-matrix least-squares refinement: function minimised $\Sigma w(|F_o| - |F_c|)^2$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$.

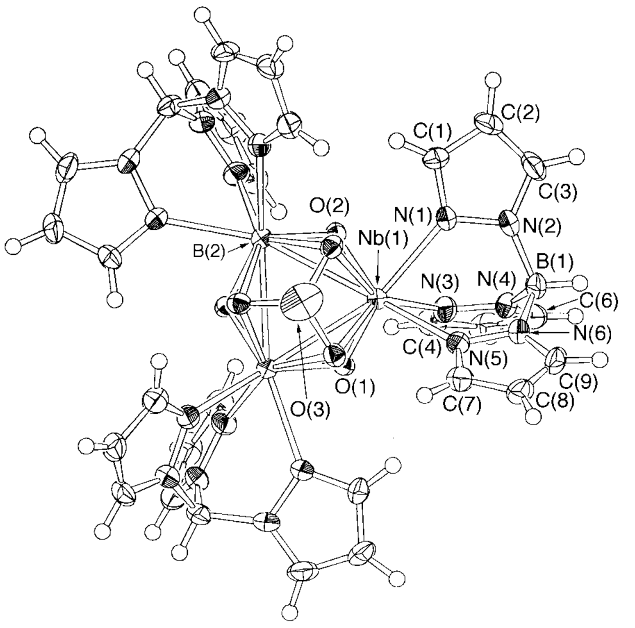


Fig. 1 View of the trimeric unit of complex **1** looking down the three-fold axis

clarity. One $HB(pz)_3^-$ ligand is co-ordinated axially to each Nb through three nitrogen atoms replacing the terminal water (chloride) ligands of the green aqueous precursor. The Nb atoms are thus formally seven-co-ordinated but highly distorted from a regular geometry. A degree of direct Nb–Nb bonding is assumed to be present. In Fig. 1 the hydrogen atoms of the $HB(pz)_3^-$ ligands have been included in idealised positions. The Nb–N [$HB(pz)_3^-$] distances vary from 2.28 to 2.33 Å and the chemically equivalent bond lengths within the $HB(pz)_3^-$ ligand are the same within experimental error and have expected values. The three pyrazolyl groups are each planar with inter-planar dihedral angles of 47.2, 62.0 and 71.2°.

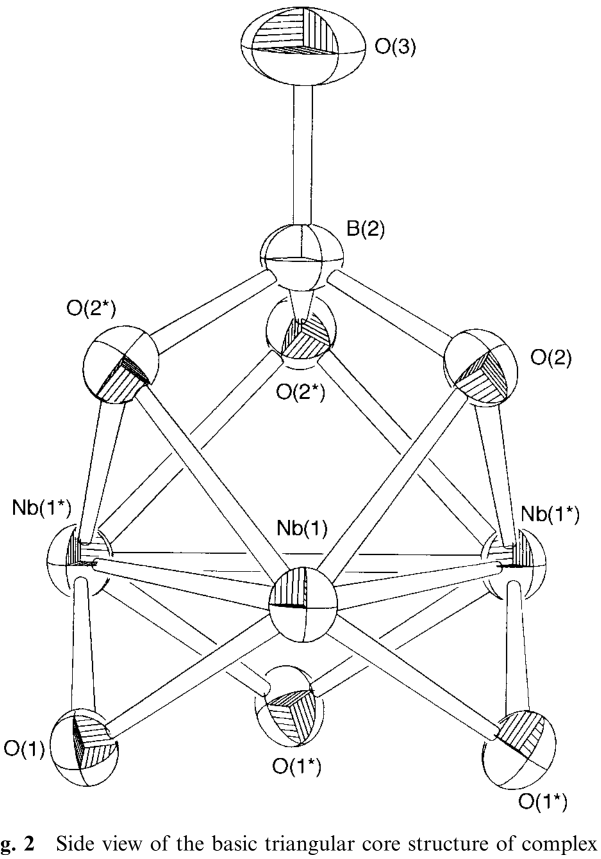


Fig. 2 Side view of the basic triangular core structure of complex **1**; the $HB(pz)_3^-$ groups have been omitted for clarity

The unique Nb–Nb distance, 2.838(1) Å, in complex **1** is comparable to distances found in several other symmetrically triangular niobium cluster compounds, *e.g.* 2.81 Å in $[Nb_3Cl_8]$ $(Nb^{II}Nb^{III}_2)$[10] and in $[Nb_3(\mu\text{-}Cl)_2(\mu\text{-}OH)(\mu\text{-}O)_3(\eta^5\text{-}C_5Me_5)_3]^+$ $(Nb^{IV}_2Nb^{V})$,[11] 2.83 Å in $[Nb_3Cl_7(PMe_2Ph)_6]$ $(Nb^{II}_2Nb^{III})$[12] and

Table 2 Selected bond lengths (Å) and (°) for complex **1**

Nb(1)–Nb(1^{i})	2.838(9)	Nb(1)–N(1)	2.328(5)
Nb(1)–O(1)	1.920(4)	Nb(1)–N(3)	2.282(5)
Nb(1)–O(1^{i})	1.964(4)	Nb(1)–N(5)	2.289(5)
Nb(1)–O(2)	2.092(4)	B(2)–O(2)	1.507(6)
Nb(1)–O(2^{ii})	2.119(4)	B(2)–O(3)	1.45(1)
Nb(1)–Nb(1)–Nb(1)	60	O(2)–B(2)–O(2^{i})	102.8(5)
Nb(1)–O(1)–Nb(1^{ii})	93.9(2)	O(2)–B(2)–O(3)	115.5(4)
Nb(1)–O(2)–Nb(1^{i})	84.7(1)		

Symmetry relations: i $-1 - x + y, -1 - x, z$; ii $-1 - y, x - y, z$.

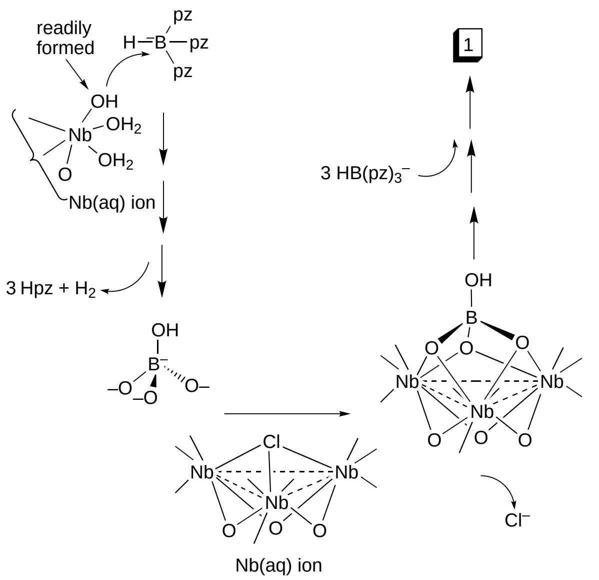
in $[Nb_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CMe)_6(thf)_3]^+$ ($Nb^{III}Nb^{IV}_2$),[13] 2.84 Å in $[Nb_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCMe_3)_6(thf)_3]^+$ ($Nb^{III}Nb^{IV}_2$),[13] 2.86 Å in $[Nb_3(\mu\text{-}Cl)_3(\mu\text{-}O)_3(\eta^5\text{-}C_5Me_5)_3]^+$ ($Nb^{IV}_2Nb^V$)[11] and 2.87 Å in $[Nb_3(\mu_3\text{-}O)_2(\mu\text{-}SO_4)_6(OH_2)_3]^{5-}$ ($Nb^{III}Nb^{IV}_2$)[13a,14] although somewhat shorter and longer Nb–Nb distances have been observed in other cases, *e.g.* 2.76 Å in $[Nb_3(\mu_3\text{-}S)(\mu\text{-}O)_3(NCS)_9]^{6-}$ ($Nb^{III}Nb^{IV}_2$),[2] 2.98 Å in $[Nb_3Cl_{10}(PEt_3)_3]^-$ (Nb^{III}_3)[12] and 3.14 Å in $[Nb_3(\mu\text{-}O)_2(\mu\text{-}OH)_2(\mu\text{-}O_2CH)_3(\eta^5\text{-}C_5Me_5)_3]$ (Nb^{IV}_3).[15]

The two unique Nb–O–Nb bridges are both nearly symmetrical with Nb–O(1) distances 1.920(4) and 1.964(4) Å and Nb–O(2) distances 2.092(4) and 2.119(4) Å. The Nb–O(1)–Nb and Nb–O(2)–Nb bridge angles are respectively 93.9(2) and 84.7(1)°.

It has not been possible to establish directly from the X-ray data whether or not any of the O atoms carry hydrogens and as such the formal oxidation state at niobium in the cluster has been unequivocally assigned. This is also not possible from an analysis of the Nb–Nb separation as demonstrated by the range of structural examples shown above. However a bond-valence sum (BVS) analysis can be used to identify the probable location of any protons. This approach uses empirical bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database up to 1985 by Brown and Altermatt.[16] Computed BVS values are 1.85, 1.87 and 0.81 for the O(1), O(2) and O(3) atoms of **1** respectively suggesting that a single proton is present on the apical O(3) atom of the capping borate but not on the bridging O atoms. The relatively large thermal parameters of the O(3) atom would also be not inconsistent with a degree of disorder in the position of a hydrogen atom about an O–H bond.

The presence of only one proton would be consistent with a formal oxidation state of $Nb^{IV}_2Nb^V$ with two cluster d electrons about the triangle. This formal oxidation state is indeed well established in triniobium clusters. For example formally $Nb^{IV}_2Nb^V$ is present in the cation $[Nb_3(\mu\text{-}Cl)_2(\mu\text{-}OH)(\mu\text{-}O)_3(\eta^5\text{-}C_5Me_5)_3]^+$ reported by Bottomley and Karslioglu.[11] In this cluster the hydroxide bridge is characterised by a significantly longer Nb–O bond (2.145 Å) and tighter Nb–O–Nb angle (<90°) than in the case of the three oxo bridging groups, Nb–O 1.920 Å and Nb–O–Nb angle >90°. These latter parameters match closely those involving the O(1) atoms of **1** giving further support for the μ-O assignment. The hydroxotrioxoborate group itself is distorted from regular tetrahedral with the apical B(2)–O(3)H bond, 1.45(1) Å, shorter than the three B(2)–O(2) bonds, 1.507(6) Å. The B–O bond length quoted for a symmetrical BO_4^{5-} group is 1.475 Å.[17]

The assignment of a formal $Nb^{IV}_2Nb^V$ oxidation state for complex **1** reflects its air-stability and markedly different electronic spectrum[1] when compared to those of highly air-sensitive d^4 $Nb^{III}Nb^{IV}_2$ clusters $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$[1,3,4] and $[Nb_3(\mu_3\text{-}S)(\mu\text{-}O)_3(NCS)_9]^{6-}$.[2] It is clearly apparent that a range of different formal oxidation states and core structures can be present contained within triangular niobium cluster complexes.



Scheme 1 Reactions leading to the formation of complex **1** from $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_{9-x}Cl_x]Cl_{4-x}$ (x = 0–4) in ethanol solvent

The basic core structure of complex **1** shown in Fig. 2, consisting of both μ- and μ_3-bridging oxygens, is indeed known[18] in a number of homotetranuclear metal cluster complexes such as the μ-selenido cluster $[\{Ti(\eta\text{-}C_5H_5)\}_4(\mu\text{-}Se)_3(\mu_3\text{-}Se)_3]$[19] and in the $[\{Mo(\eta\text{-}C_5Me_5)(\mu\text{-}O)\}_3(\mu_3\text{-}O)_3MoO_3]^-$ core of $[Mo_5(\eta\text{-}C_5Me_5)O_{11}]$[20] and $[Mo_8(\eta\text{-}C_5Me_5)O_{16}]$[21]. However **1** provides the first authentic heteronuclear example of a hydroxotrioxoborate group capping a triangular arrangement of niobiums or indeed any other metals within a simple molecular cluster. The oxoborate moiety must derive from complete hydrolysis of one of the $HB(pz)_3^-$ ligands during the complexation reaction in ethanol with the green aqua precursor. Indeed it is known that the water ligands on the green aqua cation are extremely acidic from the observation of grey hydrated hydroxide precipitation from aqueous solutions in 1.0 mol dm^{-3} CF_3SO_3H or *p*-$MeC_6H_4SO_3H$.[1] The ready formation of co-ordinated OH^- ligands on $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3]^{4+}$ (aq) is assumed largely responsible for hydrolysis of all three B–N bonds of one of the $HB(pz)_3^-$ ligands. The yield of **1** never exceeds 30% consistent with some $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3]^{4+}$ (aq) sacrificed in the hydrolysis reaction to produce hydroxotrioxoborate which then rapidly caps the trinuclear core of the remaining $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3]^{4+}$ (aq) moieties displacing the μ_3-chloro group, Scheme 1. In turn the introduction of the hard base oxoborate ligand acts to neutralise the cationic charge on the cluster and suppress further hydrolysis allowing co-ordination of remaining intact $HB(pz)_3^-$ ligands at the terminal water (chloride) positions.

Complex **2** is the first tetranuclear complex of niobium having a core structure consisting only of bridging and terminal oxo groups, Fig. 3. The only previous example of this arrangement is the rectangular $\{NbO(\mu\text{-}O)_4\}$ core lying within the structure of the decaniobate(V) anion, $[Nb_{10}O_{28}]^{6-}$.[22] Here the bond lengths are respectively Nb=O 1.73–1.8, Nb–O(μ) 1.96–2.1 Å compared with 1.737(7) [Nb(1)–O(3)] and 1.906(1) [Nb(1)–O(1)] and 1.918(3) Å [Nb(1)–O(2)] respectively for **2** here. Selected bond lengths and angles are listed in Table 3. Relatively long Nb–O distances, range 1.75–1.79 Å, are also a feature of the terminal Nb=O groups of the Mn^{IV}-containing isopolyniobate(V) anion $[Mn(Nb_6O_{19})_2]^{12-}$.[23]

The terminal Nb=O distance in complex **2** (1.737 Å) can also be compared with distances found in other Nb^V=O complexes, *cf.* 1.68(2) Å in $[NbOCl_3(MeCN)_2]$,[24] 1.70(2) Å in $[NbOCl_4]^-$,[25] 1.71(3) Å in $[NbOCl_2(OR)(bipy)]$ (R = Et or Pr^i),[26] 1.720(6) Å in $[NbO(O_2CMe)(tpp)]$ (tpp = 5,10,15,20-tetraphenylporphyrinate)[27] and 1.71, 1.66 and 1.69 Å respectively in $[NbO(C_2O_4)_3]^{3-}$,[28] $[NbO(C_2O_4)_2(OH)(OH_2)]^{2-}$[29] and $[NbO(C_2O_4)_2(OH_2)_2]^-$.[30] An interesting feature of **2** is the significantly different Nb–Nb distances, 3.81 and 3.64 Å, involved with

Table 3 Selected bond lengths (Å) and angles (°) for complex **2**

Nb(1)–Nb(1*)	3.81	Nb(1)–N(1)	2.286(9)
Nb(1)–Nb(1**)	3.64	Nb(1)–N(11)	2.380(9)
Nb(1)–O(1)	1.906(1)	Nb(1)–N(12)	2.266(9)
Nb(1)–O(2)	1.918(3)		
Nb(1)–O(3)	1.737(7)		
Nb(1)–O(1)–Nb(1*)	176.5(6)	O(1)–Nb(1)–O(2)	99.7(4)
Nb(1)–O(2)–Nb(1**)	142.8(5)	O(1)–Nb(1)–O(3)	101.8(4)
		O(2)–Nb(1)–O(3)	102.6(3)

Symmetry relations: * $1 - y, 1 - x, \frac{1}{2} - z$; ** $\frac{3}{2} - x, \frac{1}{2} - y, z$.

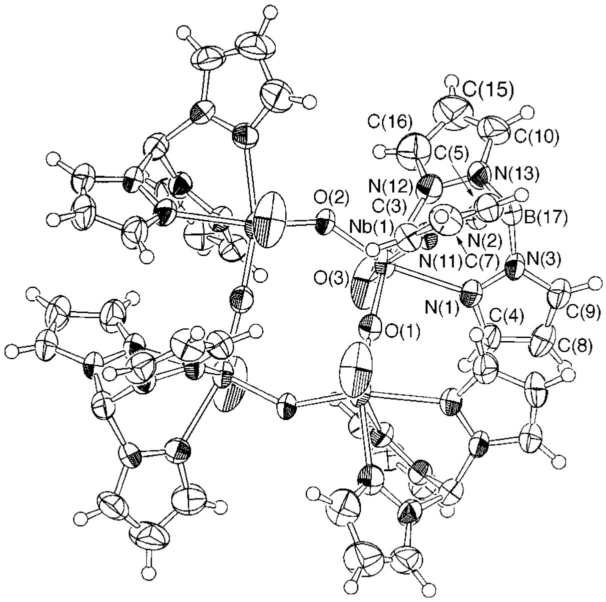
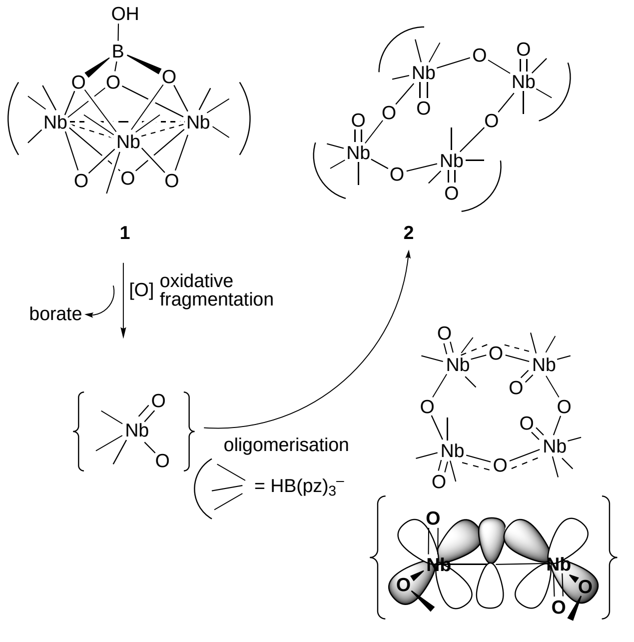


Fig. 3 View of the tetranuclear unit of complex **2** showing the two types of bridging oxo group and overall rectangular core

bridging to the O(1) and O(2) atoms respectively giving a distinctly rectangular shape to the tetranuclear core. The near linear Nb(1)–O(1)–Nb(1*) angle (≈177°) implies a significant degree of π bonding from the p_π orbitals on the O(1) atoms to the empty Nb(1) $4d_\pi$ orbitals. This is also implied from the slightly shorter Nb(1)-O(1) distance compared with that to O(2). Significant competitive π-back bonding from bridging oxo groups is also the probable reason why in the present compound and in the isopolyniobate species the terminal Nb=O bonds are relatively long. The only previously reported example of a hydridotris(pyrazol-1-yl)borate complex of niobium(v) is the oxodimethoxo complex [NbO(OMe)$_2${HB(pz)$_3$}] [ν(Nb=O) 920 cm^{-1}] reported by Hubert-Pfalzgraf and Riess[31] in 1980 for which no crystal structure has been reported.

Electrochemical studies on complex **1** show little evidence of a favourable oxidation process to niobium(v). This can now be rationalised by the requirement of a structural change to the tetranuclear core. The mechanistic pathway to **2** from **1** can be envisaged as involving initial oxidative fragmentation of **1**, with loss of the oxoborate capping group, giving monomeric Nb(=O)O{HB(pz)$_3$} units, which then rapidly reassemble into the tetranuclear core, Scheme 2. Formation of the rectangular core of **2** can be rationalised by it being the simplest oligomeric structure allowing strong π interactions through linear Nb–O–Nb groups. A triangular arrangement would not permit this to occur. Thus it is likely that the need to neutralise the high π acidity at the niobium(v) centres *via* strong π donation from both terminal and linear bridging oxo groups drives the formation of a rectangular core. Loss of the oxoborate capping ligand upon oxidation to niobium(v) is probably also a consequence of the structural change to accommodate the rectangular μ-O bridged core.



Scheme 2 Reactions leading to the formation of complex **2** from **1**. Inset: linear Nb $4d_\pi$ O p_π bonding in the tetrameric core

Complex **2** represents in effect a chelate ligand-encapsulated piece of niobium(v) oxide and has reasonable solubility in polar organic solvents. For this reason it is currently under investigation as an interesting new precursor for possible use in non-aqueous sol–gel processing of thin films of Nb_2O_5.

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