

Characterisation of a cationic triniobium aqua ion cluster and related studies †

Shehla Minhas and David T. Richens*

School of Chemistry, University of St. Andrews, Purdie Building, North Haugh, St. Andrews KY16 9ST, UK

A green air-sensitive niobium cation has been characterised in acidic aqueous solutions following Dowex cation-exchange column chromatography of hydrolysed solutions of $[\text{NbCl}_3(\text{dme})]$ (dme = 1,2-dimethoxyethane) in aqueous HCl. Redox titrations and oxygen-17 NMR studies on the green ion suggest the presence of the incomplete cuboidal structure $[\text{Nb}_3(\mu_3\text{-Cl})(\mu\text{-O})_3(\text{OH}_2)_9]^{3+}$ ($\text{Nb}^{\text{III,IV,IV}}$). Air-free solutions in HCl, $\text{CF}_3\text{SO}_3\text{H}$ and *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}$ are stable for weeks frozen at -18°C but the use of HClO_4 results in fairly rapid oxidation to colourless Nb^{V} . Water-exchange kinetic studies (use of ^{17}O NMR) have identified two distinct types of water ligand consistent with the incomplete cuboidal triangular structure. Those water ligands *trans* to the capping (Cl) atom (one per Nb) ($k^{298} = 8.3 \times 10^{-3} \text{ s}^{-1}$) are significantly more inert than those *trans* to the bridging oxo groups (two per Nb) ($k^{298} = 352 \text{ s}^{-1}$). The reaction products obtained by treatment of the green ion with aqueous methanolic NCS^- , $[\text{Nb}^{\text{III,IV,IV}}_3(\mu_3\text{-S})(\mu\text{-O})_3(\text{NCS})_9]^{6-}$ (S^{2-} deriving from NCS^-), and with aqueous ethanolic hydridotris(pyrazol-1-yl)borate, $\text{HB}(\text{pz})_3^-$, $[\text{Nb}_3(\mu_3\text{-BO}_4)\{\mu\text{-}(\text{O,OH})\}_3\{\text{HB}(\text{pz})_3\}_3]$ [the BO_4^{5-} ligand deriving from the hydrolysis of $\text{HB}(\text{pz})_3^-$], suggest the ready formation of a range of triangular Nb_3 cluster cores with different complexing ligands.

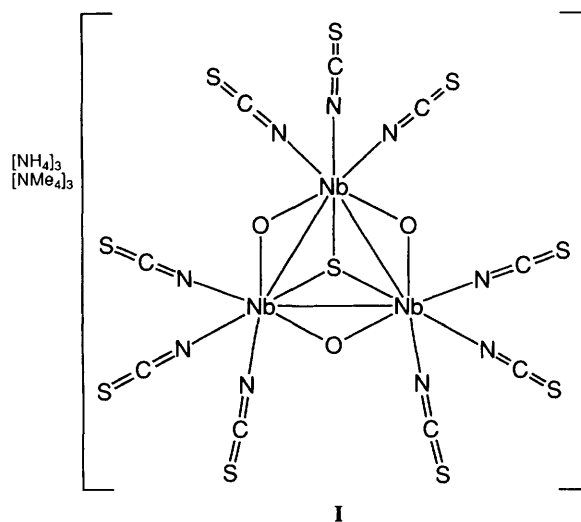
In 1986 Cotton *et al.*¹ reported isolation of a green cationic species following treatment of $[\text{Nb}_2\text{Cl}_6(\text{tht})_3]$ (tht = tetrahydrothiophene)² with aqueous HCl and subsequent cation-exchange chromatography. Evaporation of the resulting green HCl solutions to dryness followed by dissolution in methanol (or ethanol) and treatment with NH_4NCS and NMe_4Cl allowed the structural characterisation of the triangular triniobium(III,IV,IV) complex $[\text{NH}_4]_3[\text{NMe}_4]_3[\text{Nb}_3(\mu_3\text{-S})(\mu\text{-O})_3(\text{NCS})_9]$ **I**. It was proposed that the green species contained the cation $[\text{Nb}_3(\mu_3\text{-X})(\mu\text{-O})_3(\text{OH}_2)_9]^{3+}$ ($\text{X} = \text{O}$ or S).¹ We have been interested in further characterising this green species as providing potentially the first example of an authentic niobium oxoaqua cation. Moreover the basic M_3X_{13} cluster unit present in **I** is the same as that present in the known family of aqua ion clusters $[\text{M}_3(\mu_3\text{-X})(\mu\text{-X})_3(\text{OH}_2)_9]^{4+}$ ($\text{X} = \text{O}$ or S , $\text{M} = \text{Mo}$ or W).³ Further examples of the M_3X_{13} unit are provided by $[\text{Nb}_3\text{Cl}_{10}(\text{PET}_3)_3]^-$ and $[\text{Nb}_3\text{Cl}_7(\text{PET}_2\text{Ph})_6]^-$.⁴

The capping sulfur atom in **I** could conceivably have derived from tht or NCS^- . To ensure the likely synthesis of an 'all-oxo' species we searched for an alternative non-sulfur-containing lead-in compound. We report here the results of studies conducted on the green cationic species obtained following Dowex cation-exchange chromatography of hydrolysed solutions of the complex $[\text{NbCl}_3(\text{dme})]^{5-}$ (dme = 1,2-dimethoxyethane) in aqueous HCl. We believe that this green species is the first example of an authentic cationic niobium 'aqua ion' present as a trinuclear oxo-bridged cluster. Water-exchange and substitution reactions at the terminal water ligands of the cluster ion have been followed by ^{17}O NMR spectroscopy using ^{17}O -enriched samples. Treatment of the green species with methanolic NCS^- gives $[\text{Nb}_3(\mu_3\text{-S})(\mu\text{-O})_3(\text{NCS})_9]^{6-}$ **I**. However, treatment with aqueous ethanolic potassium hydridotris(pyrazol-1-yl)borate, $\text{K}[\text{HB}(\text{pz})_3]$, gives the unusual borate-capped trinuclear complex $[\text{Nb}_3(\mu_3\text{-BO}_4)\{\mu\text{-}(\text{O,OH})\}_3\{\text{HB}(\text{pz})_3\}_3]$.

Experimental

Preparation of solutions of the green niobium 'aqua ion'

All manipulations and column chromatography were carried



out under an argon atmosphere using stainless-steel needles, syringes, rubber septum caps and narrow-gauge Teflon tubing as described in previous papers.⁶ Samples of $[\text{NbCl}_3(\text{dme})]$ were either prepared by reduction of freshly sublimed NbCl_5 (Aldrich) in anhydrous dme with tri-*n*-butyltin hydride⁵ or obtained directly from Aldrich. Samples of the complex (≈ 0.5 g) were treated with deoxygenated concentrated HCl (5.0 cm^3) wherein a deep bluish green solution was formed. Following filtration to remove any undissolved material the resulting solution was diluted to 0.5 mol dm^{-3} in $[\text{H}^+]$ and loaded onto a deoxygenated column ($6 \times 1 \text{ cm}$) of Dowex 50W X2 cation-exchange resin (200–400 mesh size) during which the solution took on a more brownish green appearance. The column, which became saturated with a dark brownish green band, was washed with both 0.5 and 1.0 mol dm^{-3} HCl (50 cm^3 of each) prior to elution of the green niobium aqua species with 4.0 mol

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dm^{-3} HCl. Much brownish green material remained on the column, some of which was eluted with concentrated HCl. The 4.0 mol dm^{-3} HCl eluents were then evaporated to dryness on a vacuum line at 10^{-2} Torr (*ca.* 1.33 Pa) with gentle heating (water-bath at 60°C) to leave a dark brownish green residue, which readily dissolved to make concentrated stock solutions as high as 0.6 mol dm^{-3} in Nb in the desired acid of choice [HCl, $\text{CF}_3\text{SO}_3\text{H}$ or *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}$ (Hpts)]. Treatment of the green ion with HClO_4 gave rise to slow but complete oxidation to colourless Nb^{V} over a 2 h period at 25°C .

Oxygen-17-enriched solutions of the green niobium aqua ion were prepared as follows. Aqueous solutions of HCl enriched in ^{17}O were prepared by saturating 2.0 cm^3 volumes of 10 atom% H_2^{17}O (Yeda, Israel) with HCl gas followed by treatment with $[\text{NbCl}_3(\text{dme})]$ (0.5 g) and the resulting green solution purified by cation-exchange chromatography as above. Rapid exchange of the co-ordinated waters back to natural abundance in ^{17}O (0.037 atom %) was found to occur during the column treatment and so re-enrichment of these was performed by addition of further quantities of H_2^{17}O along with the desired acid in the final dissolution of the chloroaqua residue.

Niobium was determined gravimetrically as Nb_2O_5 following aerial oxidation of dilute (0.5 mol dm^{-3}) Hpts solutions of the aqua ion to Nb^{V} , boiling to coagulate the precipitated hydrated Nb_2O_5 , filtration and finally ignition to the anhydrous pentaoxide in an oven at 150°C . Various reported analytical methods based upon either colorimetry or atomic absorption proved unsatisfactory due to chronic matrix effects. Electronic spectra were obtained in 1.0 cm^3 quartz cuvettes using a Perkin-Elmer Lambda 5G spectrophotometer. Cyclic voltammograms were recorded using a Princeton Applied Research model 170 electrochemistry system with built-in Houston X-Y plotter. A standard three-electrode design was employed using either a mercury-cup or glassy-carbon working electrode, platinum wire counter and saturated calomel (SCE) reference electrodes. Magnetic susceptibility measurements were made at room temperature using a Johnson Matthey minibalace. Fast atom bombardment mass spectra were recorded at the EPSRC National Service at the University of Wales, College of Swansea using a 3-nitrobenzyl alcohol matrix.

NMR spectroscopy

Oxygen-17 NMR spectra were obtained on Bruker AM-300 and MSL-500 spectrometers operating at 40.56 and 67.79 MHz respectively using sealed 10 mm tubes. For some kinetic experiments normal plastic cap sealed tubes flushed with argon gas were employed. Spectra were obtained over a sweep range of 62 500 Hz following transformation of typically 50,000–130,000 accumulations (90° pulse width 27 μs) using 100 Hz line broadening. Spline functions were applied to correct for the rolling baseline. Manganese(II), added as $[\text{Mn}(\text{OH}_2)_6]\text{X}_2$ ($\text{X} = \text{CF}_3\text{SO}_3^-$ or Cl^-) (0.1 mol dm^{-3}), was added to relax efficiently the ^{17}O resonance line of bulk water thus enabling monitoring of the region $\delta \pm 50$ from bulk water, referenced as $\delta 0$.⁷ Variable-temperature linewidth measurements were carried out between 10 and 65°C on the AM-300 instrument. The probe temperature was calibrated by using the ^1H NMR resonances of an ethylene glycol standard. Niobium-93 NMR spectra were obtained using a standard high-resolution probe on the MSL-500 spectrometer operating at 122.41 MHz and at 40°C over a sweep range of 500 000 Hz following transformation of $\approx 50,000$ accumulations (90° pulse 18 μs) using 500 data points. The spectra were referenced to the chemical shift obtained from a solution of $\text{Cs}[\text{NbCl}_6]$ in dry acetonitrile ($\delta 0$). Proton and ^{13}C solution NMR spectra were recorded *vs.* SiMe_4 on solutions in CDCl_3 or CD_2Cl_2 in standard 5 mm NMR tubes at 25°C using the Bruker AM-300 spectrometer.

Other reagents

Trifluoromethanesulfonic acid (triflic acid), $\text{CF}_3\text{SO}_3\text{H}$ (Fluorochem), was used as supplied; $[\text{Mn}(\text{OH}_2)_6][\text{O}_3\text{SCF}_3]_2$ was prepared by neutralisation of the carbonate with aqueous triflic acid followed by recrystallisation twice from water. Potassium hydridotris(pyrazol-1-yl)borate, $\text{K}[\text{HB}(\text{pz})_3]$, was prepared using standard published methods.⁸ All other solvents were of reagent grade quality.

Reaction of the green niobium aqua cation with $\text{K}[\text{HB}(\text{pz})_3]$

A sample of the residue (0.3 g) obtained by evaporation of HCl solutions of the green niobium cation to dryness was dissolved in deoxygenated ethanol (10 cm^3) giving rise to a greenish brown solution. An ethanolic solution of $\text{K}[\text{HB}(\text{pz})_3]$ (0.38 g in 10 cm^3) was then added causing an immediate change to deep golden brown. This solution was filtered and left to stand under argon at room temperature for several days. After this time a crop of air-stable red-brown diamagnetic microcrystals were deposited (overall yield $\approx 30\%$). These were found to be only poorly soluble in ethanol and were thus washed by decantation of the bulk ethanol solution and treatment with fresh aliquots of deoxygenated ethanol. However recrystallisation by diffusion of diethyl ether into a CH_2Cl_2 solution afforded pinkish red crystals. The FAB mass spectral, microanalytical and NMR data showed them to consist of the μ_3 -borate-capped cluster $[\text{Nb}_3(\mu_3\text{-BO}_4)\{\mu\text{-(O,OH)}\}_3\{\text{HB}(\text{pz})_3\}_3]\cdot\text{EtOH}\cdot\text{H}_2\text{O}$ (M_r 1105.2) [Found: C, 31.55; H, 3.35; N, 22.40. Calc. for $\text{C}_{29}\text{H}_{38}\text{B}_4\text{N}_{18}\text{Nb}_3\text{O}_9$: C, 31.50; H, 3.45; N, 22.80%]; positive-ion FAB mass spectrum M^+ 1070 [$M_r - 36$ (H_2O)]; δ_{H} (CDCl_3) 1.07 (3 H, t) and 3.51 (2 H, q) (solvated EtOH), 4.7 (br, H_2O) (removed with D_2O), 7.27 (1 H, s, CHCl_3), 6.15 (9 H, m), 7.68 (9 H, m) and 8.34 (9 H, m) (pyrazol-1-yl); δ_{C} (CD_2Cl_2) 18.5 (1 C, s) and 56.3 (1 C, s) (solvated EtOH), 54.2 (1 C, t, $\text{CD}_2\text{Cl}_2\text{-CH}_2\text{Cl}_2$), 105.6 (9 C, s), 136.5 (9 C, s) and 144.9 (9 C, s) (pyrazol-1-yl). The crystal structure of this complex has confirmed the presence of the μ_3 -borate capping ligand as well as the loosely bound molecules of solvent and will be reported in a subsequent paper. Solutions of the red complex in CH_2Cl_2 or CHCl_3 are non-conducting.

Reaction of a methanolic solution of the green residue with $\text{K}[\text{HB}(\text{pz})_3]$ in a similar manner afforded pinkish red crystals of the corresponding methanol solvate, $[\text{Nb}_3(\mu_3\text{-BO}_4)\{\mu\text{-(O,OH)}\}_3\{\text{HB}(\text{pz})_3\}_3]\cdot\text{MeOH}\cdot\text{H}_2\text{O}$ (M_r 1091.2) [Found: C, 30.45; H, 3.05; N, 22.55. Calc. for $\text{C}_{28}\text{H}_{36}\text{B}_4\text{N}_{18}\text{Nb}_3\text{O}_9$ requires C, 30.80; H, 3.30; N, 23.09%]; positive-ion FAB mass spectrum, M^+ 1056 [$M_r - 36$ (H_2O)] and 1042 [$M_r - 50$ ($\text{H}_2\text{O} + \text{MeOH}$)]; δ_{H} (CDCl_3) 3.15 (3 H, s, solvated MeOH), 4.6 (br, H_2O) (removed with D_2O); δ_{C} (CD_2Cl_2) 54.2 (solvated $\text{MeOH} + \text{CD}_2\text{Cl}_2\text{-CH}_2\text{Cl}_2$).

Results and Discussion

Characterisation of the green niobium cation

Solutions of the diamagnetic green niobium aqua ion in 4.0 mol dm^{-3} triflic acid give the electronic spectrum shown in Fig. 1. Band maxima are observed at 414 ($\epsilon = 170$) and 622 nm ($80 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ per Nb atom) with two shoulders at ≈ 320 and ≈ 500 nm. In 4.0 mol dm^{-3} HCl the two band maxima occur at 427 and 634 nm (no significant change in ϵ), the bathochromic shift being indicative of substitution of terminal water by Cl^- . In the presence of three equivalents of NCS^- (per Nb atom) a further bathochromic shift in both band maxima is observed, Fig. 1, together with an increase in intensity of the higher-energy band and a rapid rise in absorbance below 340 nm due to the appearance of an intense charge-transfer band. Solutions of the green ion rapidly reduced acidic aqueous solutions of Fe^{3+} to Fe^{2+} (oxidation to Nb^{V}) and this was used in back titrations

with solutions of $\text{Ce}^{\text{IV}}(\text{aq})$ to determine the number of reducing equivalents. From an average of three titrations, the average oxidation state of niobium was determined as $+3.65 \pm 0.02$ implying a trinuclear $\text{Nb}^{\text{III,IV,IV}}$ core, hereafter referred to as $\text{Nb}_3(\text{aq})$. This formal oxidation state is identical to that found in a number of other trinuclear niobium cluster complexes, e.g. **1**, and seems to be a common stable arrangement in niobium chemistry. Indeed cyclic voltammograms of solutions of the green ion in $4.0 \text{ mol dm}^{-3} \text{ HCl}$ failed to reveal evidence of any niobium-centred oxidation or reduction processes within the range $+1.0$ to -1.0 V (*vs.* SCE).

Oxygen-17 and niobium-93 NMR studies of $\text{Nb}_3(\text{aq})$

Solutions of $\text{Nb}_3(\text{aq})$ in $\text{CF}_3\text{SO}_3\text{H}$, fully enriched in ^{17}O , showed three resonances assignable as follows, δ 305 (bridging oxygen), 22 and -24 (bound H_2O) (ratio 1:2:1), Fig. 2, in addition to the resonance of CF_3SO_3^- at δ 159. No other resonances were observed in the range δ -200 to 1200 . The resonances at δ 22 and -24 , found to be in a 2:1 ratio, are similar in appearance to those characterising the water ligands

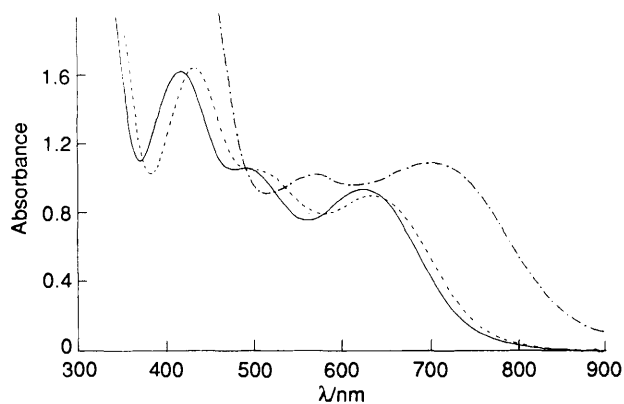


Fig. 1 Electronic spectra for solutions of $\text{Nb}_3(\text{aq})$ ($0.012 \text{ mol dm}^{-3}$ per Nb) in $4.0 \text{ mol dm}^{-3} \text{ CF}_3\text{SO}_3\text{H}$ or $4.0 \text{ mol dm}^{-3} \text{ Hpts}$ (—), $4.0 \text{ mol dm}^{-3} \text{ HCl}$ (- - -) and in the presence of 3 equivalents of NCS^- (- · -)

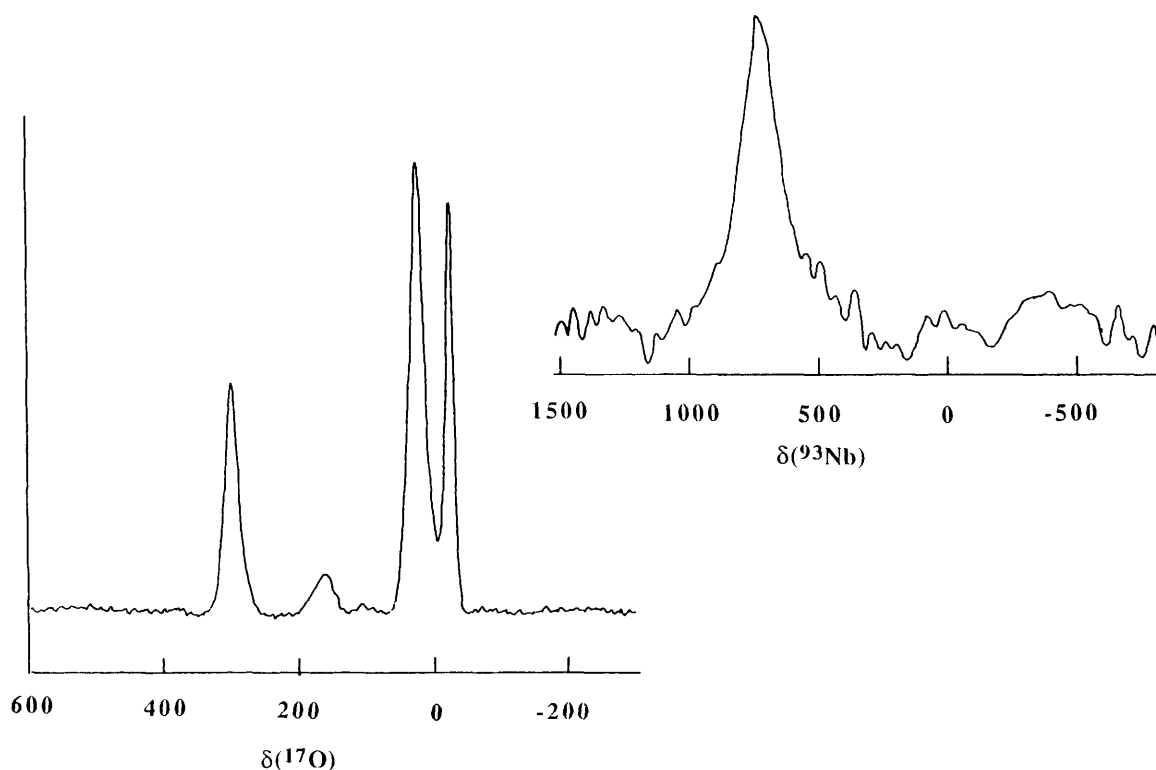


Fig. 2 The $67.79 \text{ MHz } ^{17}\text{O}$ NMR spectrum from a solution of 5 atom % ^{17}O -enriched $\text{Nb}_3(\text{aq})$ (0.1 mol dm^{-3}) in $4.0 \text{ mol dm}^{-3} \text{ CF}_3\text{SO}_3\text{H}$ containing Mn^{2+} (0.1 mol dm^{-3}). Inset: $122.41 \text{ MHz } ^{93}\text{Nb}$ NMR spectrum from the same solution

(c) and (d) on the trinuclear aqua ions $[\text{M}_3(\mu_3\text{-X})(\mu\text{-X})_3(\text{OH}_2)_9]^{4+}$ ($\text{M} = \text{Mo}$ or W , $\text{X} = \text{O}$ or S).⁹ For these latter species (for $\text{X} = \text{O}$) two additional ^{17}O NMR resonances (3:1 ratio) in the range δ 300–800 also characterised the $\mu\text{-O}$ and $\mu_3\text{-O}$ bridging oxygens respectively.¹⁰ The appearance of only one ^{17}O NMR resonance for $\text{Nb}_3(\text{aq})$ at $\delta \approx 300$, assignable to $\mu\text{-O}$, would appear to rule out the presence of a $\mu_3\text{-O}$ group. However given that the ^{17}O NMR spectrum of $\text{Nb}_3(\text{aq})$ is consistent with a structure $[\text{Nb}_3(\mu_3\text{-X})(\mu\text{-O})_3(\text{d-OH}_2)_6-$

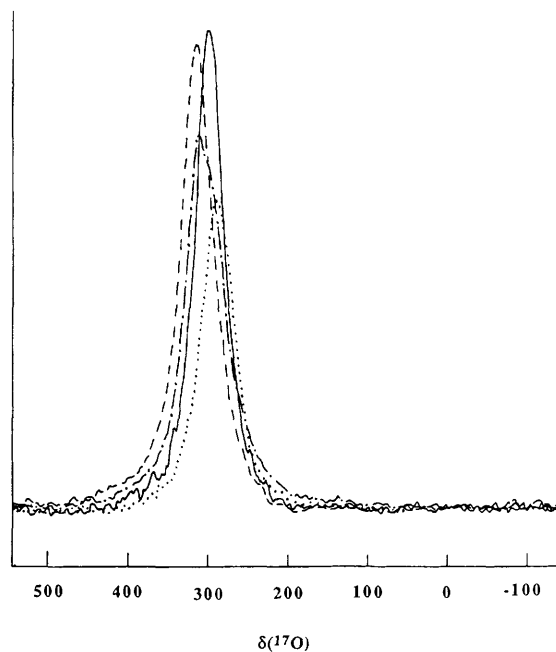
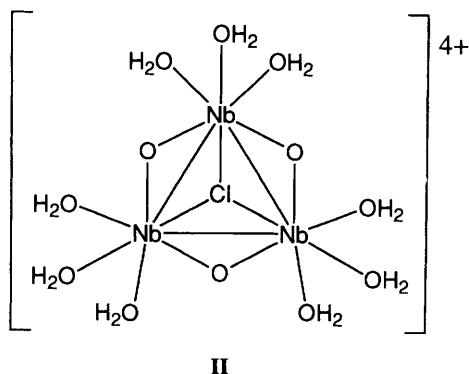


Fig. 3 The $40.56 \text{ MHz } ^{17}\text{O}$ NMR spectra from solutions ($\approx 0.1 \text{ mol dm}^{-3}$ per Nb) of 5 atom % of the $\mu\text{-}^{17}\text{O}$ -enriched Nb_3 chloroaqua residue in (i) $4.0 \text{ mol dm}^{-3} \text{ HCl}$ (—), (ii) MeOH after 15 min (- - -), (iii) MeOH after 3 h (- · -) and (iv) (iii) + 5 equivalents of NaNCS (· · ·). The solutions contain MnCl_2 (0.1 mol dm^{-3})



(*c*-OH₂)₃]⁴⁺ (¹⁷O ratio 1:2:1), alternative candidates for the μ₃-X ligand might be S or Cl, both of which are established in trimeric niobium complexes such as [Nb₃(μ₃-S)(μ-O)₃(NCS)₉]⁶⁻,¹ [Nb₃(μ₃-Cl)(μ-Cl)₃Cl₃(PEt₂Ph)₆]⁴⁺, [Nb₃(μ₃-Cl)(μ-Cl)₃Cl₆(PEt₃)₃]⁻⁴ and Nb₃Cl₈.¹¹ Sulfur can be ruled out since in the present synthesis no sulfur-containing compound was employed. Indeed the electronic spectrum of Nb₃(aq) is the same irrespective of whether [Nb₂Cl₆(tht)₃] or [NbCl₃(dme)] is employed as the lead-in. The only remaining candidate would appear to be chloride. We propose therefore that solutions of Nb₃(aq) contain the ion [Nb^{III,IV,IV}₃(μ₃-Cl)(μ-O)₃(OH₂)₉]⁴⁺ **II**.^{*} The ⁹³Nb NMR spectrum is also shown in Fig. 2, consisting of one extremely broad resonance (Δν₁ 2500 Hz) at δ ≈ 720, downfield from [NbCl₆]⁻. This suggests that the niobium atoms are valence delocalised on the NMR time-scale at room temperature.

The formation of compound **I**, possessing an Nb₃(μ₃-S)(μ-O)₃³⁺ core, following treatment of Nb₃(aq) in MeOH with an excess of NCS⁻ prompted a reinvestigation of this reaction using a ¹⁷O-enriched sample of Nb₃(aq). The results are shown in Fig. 3. The addition first of MeOH and then secondly 3 equivalents of NCS⁻ caused only a very slight shift in the μ-O resonance of Nb₃(aq), prepared from 4.0 mol dm⁻³ HCl. Similar findings are apparent upon treatment with S²⁻. Therefore it would appear that the structural changes are occurring to the μ₃-capping position only, conceivably simple replacement of μ₃-Cl by μ₃-S. In the formation of **I**¹ the origin of the μ₃-S group must be *via* abstraction of S²⁻ from NCS⁻ in the presence of H⁺.¹² (Thiocyanate has the ability to act as a mild but effective S²⁻ transfer agent in acidic solution.) This prompted investigations wherein the hydrolysis of [NbCl₃(dme)] in aqueous HCl was carried out in the presence of an excess of Na₂S·9H₂O. This resulted in solutions more olive-green in appearance which were subjected to Dowex cation-exchange chromatography. Two niobium-containing species were elutable from these solutions with aqueous 2.0 mol dm⁻³ HCl, the first being identical to that of the Nb₃(aq) species obtained above in the absence of S²⁻, whereas the second possessed an intense peak at 368 nm in addition to broad features in the region 400–700 nm, Fig. 4. Air oxidation of the olive-green fraction (to Nb^V) gave a positive test for S²⁻ [black precipitation with a solution of lead(II) acetate]. An intense peak around 360 nm also characterises [Mo₃(μ₃-S)(μ-O)₃(OH₂)₉]⁴⁺ as distinct from the μ₃-O analogue.^{3,13} A distinct shoulder at ≈ 360 nm is also a feature of the UV/VIS spectra obtained from solutions of Nb₃(aq) treated with NCS⁻, Fig. 4. Such solutions lead to the isolation of **I** containing a μ₃-S group.¹ By inference we conclude that the second olive-

* A third alternative to explain the ¹⁷O NMR results would be the absence of a capping ligand. However this situation is so far unprecedented for structures of this type and moreover would necessitate a very high charge of 5⁺ on the Nb₃(aq) core which would be inconsistent with the observed cation-exchange behaviour. By inference we therefore propose a μ₃-Cl cap.

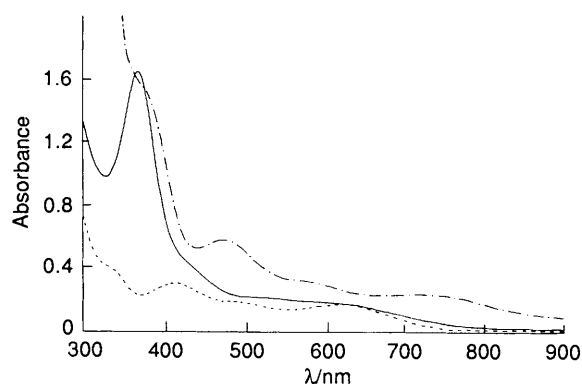


Fig. 4 Electronic spectra from solutions of (i) Nb₃(aq) (0.0025 mol dm⁻³ per Nb) in 4.0 mol dm⁻³ Hpts (—), (ii) olive-green Nb(aq) species eluted from Dowex 50W columns following hydrolysis of [NbCl₃(dme)] in 4.0 mol dm⁻³ HCl in the presence of 100 equivalents of Na₂S (---) and (iii) the Nb₃(aq) chloroqua residue in MeOH + 5 equivalents of NaNCS (-.-)

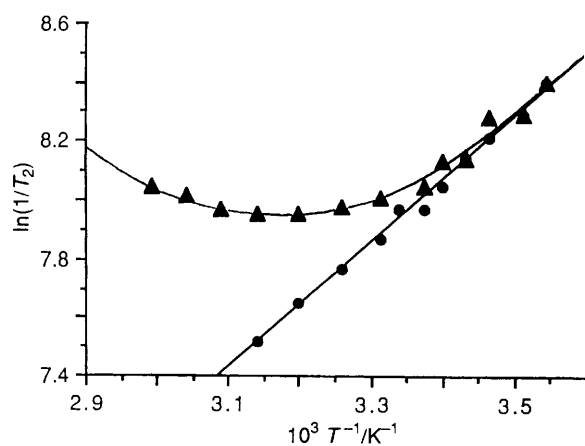


Fig. 5 Temperature dependence of the transverse relaxation times (*T*₂) for the *c*- (●) and *d*-H₂O (▲) ligands of Nb₃(aq) (0.05 mol dm⁻³) at [H⁺] 2.5 mol dm⁻³, *I* = 3.0 mol dm⁻³ (NaO₃SCF₃)

green Nb₃(aq) species eluted above is the corresponding μ₃-S ion [Nb₃(μ₃-S)(μ-O)₃(OH₂)₉]³⁺.

Water-exchange studies on Nb₃(aq)

Investigations using ¹⁷O NMR spectroscopy have shown that the two H₂O ligands of Nb₃(aq) have markedly different exchange rates. By analogy with the labels used to define the H₂O ligands on [Mo₃(μ₃-X)(μ-X)₃(OH₂)₉]⁴⁺ (X = O or S),^{3,9} the H₂O ligands (*c*) (*trans* to μ₃-Cl, δ -24) (one per Nb) are more inert than those (*d*) (*trans* to μ₃-O, δ 22) (two per Nb). Above 30 °C, the linewidth of the *d*-H₂O resonance increases whereas that for the *c*-H₂O shows quadrupolar narrowing. By assuming a similar quadrupolar relaxation energy *E*_Q for the two H₂O ligands, the exchange rate constant for the *d*-H₂O ligands, *k*_{ex}, can be extracted from the observed linewidth (Hz) (proportional to the transverse relaxation rate, 1/*T*₂) according to equation (1) where 1/*T*_{2Q} is the quadrupolar relaxation rate.

$$1/T_2(\text{obs.}) = (1/T_{2Q}) + k_{\text{ex}} \quad (1)$$

The quadrupolar relaxation component was determined from the linewidth of the *c*-H₂O ligands as a function of temperature and from the linewidth of the *d*-H₂O ligands at temperatures below 30 °C. For the temperature dependence of the quadrupolar relaxation it is normal to assume an Arrhenius relationship.¹⁴ Using only data where *k*_{ex} makes ≥ 20% contribution to 1/*T*₂, values of *k*_{ex} can be extracted from the 1/*T*₂ data as a function of temperature. Fig. 5 shows a plot of ln(1/*T*₂) vs. 10³/*T* for the two H₂O ligands of Nb₃(aq)

Table 1 Complexes known to contain trinuclear niobium cluster cores

Complex	Nb–Nb/pm	Formal oxidation state	Cluster electron no.	Ref.
$[\text{Nb}_3(\mu_3\text{-S})(\mu\text{-O})_3(\text{NCS})_9]^{6-}$	276	III,IV,IV	4	1
$[\text{Nb}_3(\mu_3\text{-Cl})(\mu\text{-Cl})_3\text{Cl}_6(\text{PEt}_3)_3]^-$	298	III,III,III	6	4
$[\text{Nb}_3(\mu_3\text{-Cl})(\mu\text{-Cl})_3\text{Cl}_3(\text{PEt}_2\text{Ph})_6]$	283	III,II,II	8	4
Nb_3Cl_8	281	III,III,II	7	11
$[\text{Nb}_3(\mu_3\text{-O})_2(\mu\text{-O}_2\text{CMe})_6(\text{thf})_3]^+$	283	III,IV,IV	4	17
$[\text{Nb}_3(\mu_3\text{-O})_2(\mu\text{-O}_2\text{CCMe}_3)_6(\text{thf})_3]^+$	284	III,IV,IV	4	17
$[\text{Nb}_3(\mu_3\text{-O})_2(\mu\text{-SO}_4)_6(\text{OH}_2)_3]^{5-}$	287	III,IV,IV	4	17a, 18
$[\text{Nb}_3(\mu_3\text{-BO}_4)\{\mu\text{-}(\text{O},\text{OH})\}_3\{\text{HB}(\text{pz})_3\}_3]$	284*	(?)	(?)	This work
$[\text{Nb}_3(\mu\text{-O})_2(\mu\text{-OH})_2(\text{O}_2\text{CH})_3(\eta\text{-C}_5\text{Me}_5)_3]$	314	IV,IV,IV	3	19

* Details of the crystal structure will be reported separately.

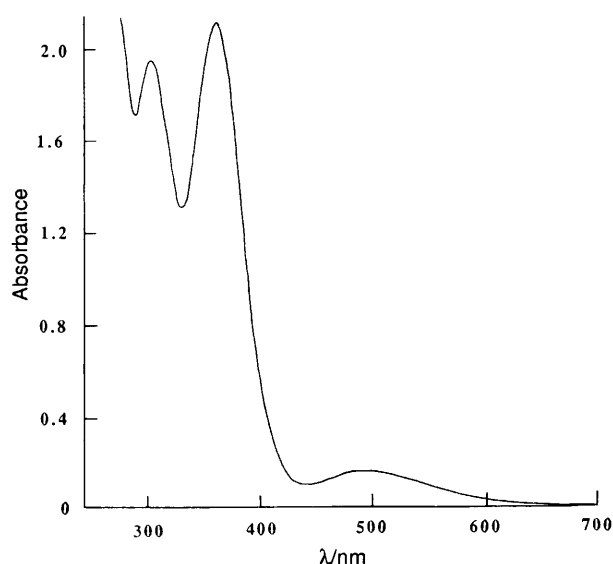


Fig. 6 Electronic spectrum from a saturated solution ($\approx 5 \text{ mmol dm}^{-3}$) of $[\text{Nb}_3(\mu_3\text{-BO}_4)\{\mu\text{-}(\text{O},\text{OH})\}_3\{\text{HB}(\text{pz})_3\}_3]$ in CH_2Cl_2

(0.05 mol dm^{-3} per Nb) at $[\text{H}^+] 2.5 \text{ mol dm}^{-3}$, $I = 3.0 \text{ mol dm}^{-3}$ (NaO_3SCF_3) from which $k_{\text{ex}}(\text{d-H}_2\text{O}) (25^\circ\text{C}) = (3.52 \pm 0.40) \times 10^2 \text{ s}^{-1}$, $\Delta H^\ddagger_{\text{ex}} = (36.8 \pm 2.2) \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger_{\text{ex}} = -72.4 \pm 6.9 \text{ J K}^{-1} \text{ mol}^{-1}$, $1/T_{2Q} = 2830 \text{ s}^{-1}$ and $E_Q = 17.7 \text{ kJ mol}^{-1}$. Contrasting with the behaviour of $[\text{Mo}_3\text{X}_4(\text{OH}_2)_9]^{4+}$ ($X = \text{O}$ or S),⁹ there is no apparent increase in the exchange rate of the d- H_2O ligands of $\text{Nb}_3(\text{aq})$ with decreasing $[\text{H}^+]$ from 2.5 to 1.25 mol dm^{-3} . Lower $[\text{H}^+]$ values $< 1.25 \text{ mol dm}^{-3}$ in CF_3SO_3^- or pts^- media cannot be tolerated owing to precipitation of a grey solid hydroxide. For this reason it has not thus far been possible to carry out a full $[\text{H}^+]$ -dependent study over a wider $[\text{H}^+]$ range for further evaluation. Much higher ^{17}O enrichments ($\geq 50\%$), so as to access a lower range of niobium concentrations, may ultimately be needed. The magnitude of the rate constant for exchange at the d- H_2O ligands is, however, in agreement with the rapid spectral changes observable upon treatment of the $\text{Nb}_3(\text{aq})$ ion with e.g. NCS^- .

Water exchange on the more inert c- H_2O ligands, *trans* to the capping ligand, was monitored by conventional means following rapid injection of 1 cm^3 of 10 atom % H_2^{17}O , containing Mn^{2+} , into a solution of $\text{Nb}_3(\text{aq})$ (0.2 mol dm^{-3}) in $5.0 \text{ mol dm}^{-3} \text{ CF}_3\text{SO}_3\text{H}$ to achieve a final ionic strength of 3.0 mol dm^{-3} . The rate constant was computed by fitting a standard exponential function to the growth in the height of the bound c- H_2O resonance as a function of time (3000 transients collected at a 33 s time interval). The resonance line of the rapidly exchanged d- H_2O served as a convenient internal reference. For the above condition $k_{\text{ex}}(\text{c-H}_2\text{O}) (25^\circ\text{C}) = (8.3 \pm 1.7) \times 10^3 \text{ s}^{-1}$.

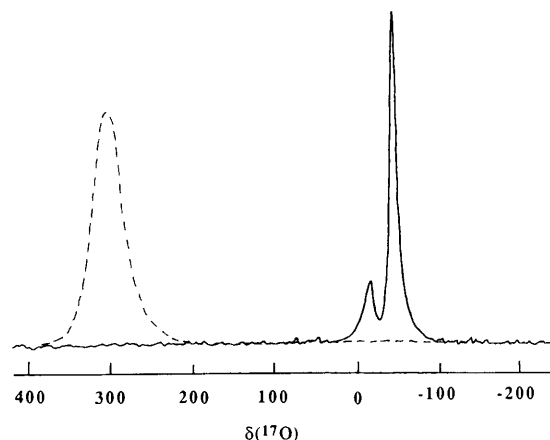


Fig. 7 The 40.56 MHz ^{17}O NMR spectrum of the enriched niobium chloroaqua residue ($\approx 0.1 \text{ mol dm}^{-3}$ per Nb) in methanol (---) and following treatment with 3 equivalents of $\text{K}[\text{HB}(\text{pz})_3]$ (—). Solutions contain MnCl_2 (0.1 mol dm^{-3})

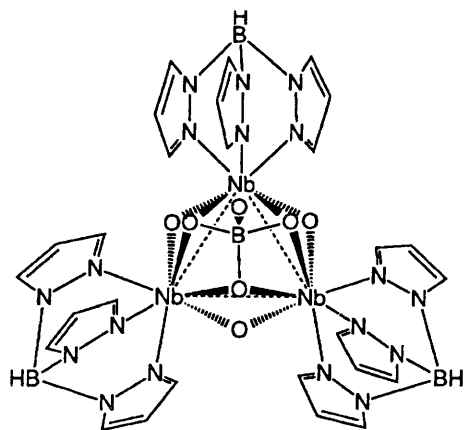
s^{-1} . The 10^4 -fold difference in rate constants for exchange between the c- and d- H_2O is interesting in view of the lack of detection of a conjugate-base labilising pathway⁹ for the d- H_2O ligands.

The low value of $\Delta H^\ddagger_{\text{ex}}$ and negative value of $\Delta S^\ddagger_{\text{ex}}$ coupled with the absence of an $[\text{H}^+]$ dependence contrasts with the higher ΔH^\ddagger and positive ΔS^\ddagger relevant to the dissociatively activated water-ligand substitution reactions on triangular Group 6 M^{IV}_3 clusters such as $[\text{Mo}_3(\mu_3\text{-S})(\mu\text{-S})(\text{OH}_2)_9]^{4+}$ ⁹ (conjugate-base pathway) and $[\text{Mo}_3(\mu_3\text{-O})(\mu\text{-O}_2\text{CMe})_6(\text{OH}_2)_3]^{2+}$.¹⁵ The $\text{Nb}^{\text{III,IV,IV}}$ triangular core structure has only four cluster d electrons per M_3 unit, as opposed to six for Mo^{IV}_3 , and as such it is electron deficient. This is a feature which might favour an associative process.¹⁶ The electron deficiency may also be responsible for the observed lability within the triangular Nb_3 framework as shown by the ready formation of a range of bridging-atom core structures (see Table 1).*

Relationship of $\text{Nb}_3(\text{aq})$ to the complex $[\text{Nb}_3(\mu_3\text{-BO}_4)\{\mu\text{-}(\text{O},\text{OH})\}_3\{\text{HB}(\text{pz})_3\}_3]\cdot\text{ROH}$ ($\text{R} = \text{Me}$ or Et)

The electronic spectrum of the red crystals dissolved in CH_2Cl_2 , Fig. 6, is markedly different from that of $\text{Nb}_3(\text{aq})$ and the products obtained upon treatment with NCS^- or S^{2-} . Figs. 1 and 3, reflecting the differing cluster cores and possibly

* It was found in further experiments that ^{17}O enrichment of the $\mu\text{-O}$ groups of $\text{Nb}_3(\text{aq})$ could be followed at temperatures above 40°C . From one run conducted at 45°C , $[\text{H}^+] 2.5 \text{ mol dm}^{-3}$, $I = 3.0 \text{ mol dm}^{-3}$ (NaO_3SCF_3), $k_{\text{ex}}(\mu\text{-O})$ was estimated to have a value $\approx 7 \times 10^5 \text{ s}^{-1}$.



III

differing formal oxidation states for niobium. Marked changes are also apparent in the ^{17}O NMR spectrum upon treatment of an enriched methanolic solution of the green $\text{Nb}_3(\text{aq})$ residue with $\text{K}[\text{HB}(\text{pz})_3]$. Here the single broad $\mu\text{-O}$ resonance of the green cation at δ 300 is replaced by two sharper ^{17}O resonances occurring at δ -17 and -45, Fig. 7. The presence of the capping borate ligand is presumed to derive from hydrolysis of a pyrazolylborate ligand. The formal oxidation state at niobium within the red $\text{HB}(\text{pz})_3^-$ complex has not been independently verified. It is not necessarily straightforward to establish the formal oxidation states in heavy-atom cluster complexes of this type from elemental analysis, FAB mass spectrometry or even a crystal structure since positionally disordered protons (*e.g.* on bridging oxo groups) are often difficult to detect. Formal oxidation states could range from $\text{Nb}^{\text{IV.V.V.}}_3$ (three bridging oxo groups present) to $\text{Nb}^{\text{III.IV.IV}}_3$ (three bridging hydroxo groups). The structure of the red complex is shown in III.

Many different formal oxidation states are represented in trinuclear cluster complexes (Table 1). The $\text{Nb}^{\text{III.IV.IV}}_3$ or Nb^{IV}_3 are the commonly observed oxidation states when hard donor ligands such as chloride and oxide are present (Table 1). The introduction of softer donors such as phosphines can stabilise lower states such as d^6 Nb^{III}_3 , $[\text{Nb}_3\text{Cl}_{10}(\text{PET}_3)_3]^-$ and d^8 $\text{Nb}^{\text{III.II.II}}_3$, $[\text{Nb}_3\text{Cl}_7(\text{PET}_2\text{Ph})_6]$. The existence of a range of μ_3 -capping groups, O, Cl, S and now borate (BO_4^{5-}), is a feature of trinuclear cluster complexes (Table 1) and may be reflective of a general lability in the core structure resulting from the d-electron deficiency. This is further apparent in the measurable exchange rate for the oxo groups of green $\text{Nb}_3(\text{aq})$ contrasting with the inertness shown by the oxo groups of trinuclear d^6

clusters, *e.g.* those of Mo^{IV} and W^{IV} [$t_{1/2}$ (25 °C) for exchange on $\text{Mo}_3\text{O}_4^{4+}(\text{aq}) \approx 1\text{--}2$ years 10].

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