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Structural parameters for the incomplete cuboidal cluster cation: $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ in solutions of acid hydrolysed trivalent niobium from Nb K edge EXAFS

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A niobium K edge EXAFS study on the green solutions obtained following hydrolysis of $NbCl_3$(dme) in aqueous non-oxidising strong acids has shown that the major species resulting in these solutions is the incomplete cuboidal chloride-capped triangular niobium cation, $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$.

We have reported previously on the isolation and characterisation of the air-sensitive cationic species present within the green aqueous solutions that result following the aqueous acid hydrolysis of trivalent niobium complexes such as $[NbCl_3$-(dme)]^{1,2} and $[Nb_2Cl_6(THT)_3]$ (THT = tetrahydrothiophene).[3] This species was first reported by Cotton and co-workers in the mid 1980s.[3] Similar green solutions have also recently been reported to result from zinc reduction of $NbCl_5$ in HCl–ethanol mixtures.[4] A combination of redox titrations and oxygen-17 labelling NMR studies following cation-exchange column purification has provided strong indications that the principal species present in these solutions is an incomplete triangular cluster ion of proposed structure $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ [delocalised Nb(III,IV,IV)].[1] Related work has shown that the putative chloride-capping ligand in the green ion can be readily replaced by *e.g.* sulfur, as in the complex $[NH_4]_3[NMe_4]_3[Nb_3(\mu_3\text{-}S)(\mu\text{-}O)_3(NCS)_9]$,[3] or hydroxotrioxoborate, as in $[Nb_3\{\mu_3\text{-}BO_3(OH)\}(\mu\text{-}O)_3(HBpz_3)_3]$ (pz = pyrazol-1-yl).[2] In the continuing absence of definitive X-ray structural data on the green cation we have carried out a niobium K edge EXAFS investigation on concentrated solutions of the green ion in CF_3SO_3H solutions. The findings have provided compelling evidence for the existence of the cluster $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ in these solutions following comparisons with a corresponding molybdenum K edge EXAFS study recently carried out on the structurally analogous incomplete cuboidal trinuclear cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ under similar conditions.[5]

A concentrated sample of the green niobium cation (0.06 mol dm^{-3} per Nb_3) in 3.0 mol dm^{-3} CF_3SO_3H was prepared as described previously[1,2] following chromatographic elution with aqueous HCl, evaporation of the HCl eluates under vacuum and dissolution of the resulting chloride salt in aqueous 3.0 mol dm^{-3} CF_3SO_3H. Samples were then loaded into a specially designed Perspex sample cell contructed with polyester (Mylar) windows for EXAFS measurements.[5,6]

The EXAFS spectra were collected on the Wiggler 1 beam line station 9.2 at the Synchrotron Radiation Source at the UK CLRC Daresbury Laboratory operating at 2 GeV (eV $\approx 1.602 \times 10^{-19}$ J) and 200 mA. The station was equipped with a water cooled harmonic rejecting double crystal Si(220) monochromator and mixtures of argon and helium gas ion chambers for measuring incident (I_o) and transmitted (I_t) beam intensities respectively, and a 13 element Ge fluorescence detector manufactured by Canberra. Data were recorded at the metal K edge in fluorescence mode. For each sample four or five scans were recorded and combined to improve signal to noise. The sample temperature was 25.0 ± 0.5 °C.

The suite of programs used to analyse the EXAFS data was that provided by the CLRC Daresbury Laboratory.[7] The raw EXAFS data were processed using the program EXCALIB and the position of the absorption edge was determined from the derivative of the spectrum using EXBROOK. This program was also used to carry out background subtraction in order to extract the EXAFS function $\chi(k)$. A k^3 weighting was used to enlarge the oscillations at large k. These oscillations are then Fourier transformed to give a quasi-radial distribution function.

Fitting of the incomplete cuboidal triangular structure was carried out with the EXCURV 92[8] program using curved wave theory and employing Hedin–Lindquist ground states and von Barth exchange potentials[9] to calculate appropriate phase shifts along with typical M–O, M–Cl, M–S and M–M distances from crystallographic data. The quality of fit is reported relative to the discrepancy index, R, and the goodness of fit relative to the fit index, *FI*.[10] The energy independent amplitude reduction factor (AFAC)[8] is a measure of the proportion of the electrons which contribute to an EXAFS-type scatter. It allows for the reduction in amplitude due to the presence of multiple excitations and is usually set to be in the range 0.7–0.9. During fitting the Debye–Waller factor ($2\sigma^2$) and the occupation number (N) were independently refined due to a high correlation.

Comparative data taken from solutions of the green niobium cation and from similarly concentrated solutions of $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3^{4+}$(aq) (0.06 mol dm^{-3}) in 2.5 mol dm^{-3} $HClO_4$, prepared in a similar manner,[5] is shown in Fig. 1. An excellent fit to the unfiltered metal K edge EXAFS is found in each case for an incomplete cuboidal triangular structure $[M_3(\mu_3\text{-}X)(\mu\text{-}O)_3(OH_2)_{9-n}Cl_n]^{(4-n)+}$ (X = S for M = Mo; X = Cl for M = Nb). For both compounds the EXAFS data refines very well to a four shell model consisting of two oxygens atoms (μ-O) at 1.91 (Mo), 2.04 Å (Nb); three terminal ligands (H_2O or Cl^-) at 2.16 (Mo), 2.22 Å (Nb); two heavy metal atoms at 2.60 (Mo), 2.78 Å (Nb) and one capping third period atom at 2.34 (S in the case of the Mo cluster), 2.49 Å (Cl in the case of the Nb cluster) with estimated errors ±0.03 Å, Table 1. The calculated bond distances[5] for the $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3^{4+}$ core have been shown to be in excellent agreement with those obtained from two crystal structures of complexes of the $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3^{4+}$ core with L-cysteinate and hydrogen nitrilotriacetate reported by Shibahara *et al.*[11] and this gives weight to the reliability of the Hedin–Lindquist exchange potentials and von Barth ground states used in this work for calculating appropriate phase shifts for the refinement of the EXAFS data on these aqueous species. The similarity in the overall EXAFS patterns and Fourier transformed data apparent for both species in Fig. 1, provides compelling evidence for the presence of the $Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3^{4+}$ core in solutions of the green niobium cation.

Niobium K edge EXAFS data were subsequently taken from a more diluted sample of the green cation (0.01 mol dm^{-3} per

Table 1 Comparison of metal K edge EXAFS data on aqueous $[M_3(\mu_3\text{-}X)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ species

Species	M–O(μ)/Å	M–X(μ₃)/Å	M–M/Å	M–OH₂/Å
$[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ (0.06 mol dm^{-3} per Mo$_3$ in 2.5 mol dm^{-3} HClO$_4$ solution)				
Refined EXAFS distances (*ca.* ±0.03 Å)	1.91	2.34(S)	2.60	2.16
Occupation numbers (*N*)	2.0	1.0	2.0	3.0
Debye–Waller factors ($2\sigma^2$)	0.008	0.009	0.004	0.009
AFAC = 0.77; *R* (%) = 23.0351;* *FI* = 0.000 29.*				
Green niobium aqueous cation (0.06 mol dm^{-3} per Nb$_3$ in 3.0 mol dm^{-3} CF$_3$SO$_3$H solution)				
Refined EXAFS distances (*ca.* ±0.03 Å)	2.04	2.49(Cl)	2.78	2.22
Occupation numbers (*N*)	2.0	1.0	2.0	3.0
Debye–Waller factors ($2\sigma^2$)	0.005	0.007	0.006	0.009
AFAC = 0.78; *R* (%) = 30.5547;* *FI* = 0.000 55.*				

* *R* is the discrepancy index = $\int|\chi^{th}(k) - \chi^{exp}(k)|k^3\,dk/\int|\chi^{exp}(k)|k^3\,dk \times 100\%$,[10] which measures the quality of fit. *FI* is the fit index = $\Sigma(k_i)^n(\chi_i^{th} - \chi_i^{exp})$[10] which measures the goodness of fit where χ^{th} and χ^{exp} are the theoretical and experimental EXAFS respectively.

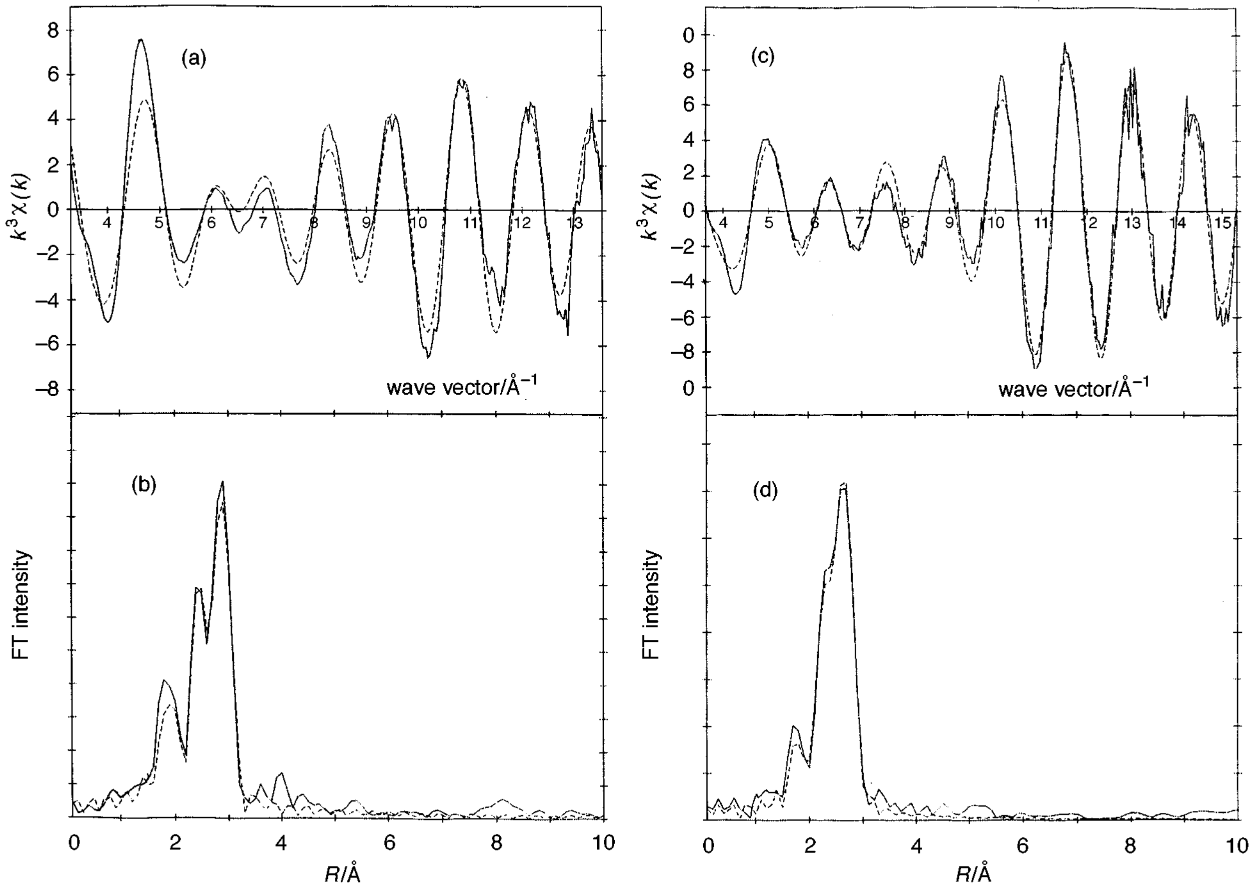


Fig. 1 Experimental (——) and calculated (-----) metal K edge EXAFS spectra and Fourier transformed data from (a, b) the green niobium aqueous cation (0.06 mol dm^{-3} per Nb$_3$ in 3.0 mol dm^{-3} CF$_3$SO$_3$H and (c, d) $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ (0.06 mol dm^{-3}) in 2.5 mol dm^{-3} HClO$_4$ (phase shifts calculated using Hedin–Lindquist ground states and von Barth exchange potentials)

Nb$_3$) in 3.0 mol dm^{-3} CF$_3$SO$_3$H. This was to check whether the rather large Debye–Waller factors, coupled with rather long distances to the terminal atoms particularly in the case of the niobium ion (Table 1), could be due to the presence of some co-ordinated Cl$^-$ at the terminal sites as a result of incomplete aquation in solutions of the chloride salt at the higher concentrations (≈0.06 mol dm^{-3}). The refined EXAFS data are shown in Fig. 2 and Table 2. The poorer signal to noise ($R = 34.8387$, $FI = 0.000\,66$) reflected the lower niobium concentration. However the four backscattering shells around each niobium atom were more easily discernible fitting well to the fully aquated cluster $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ with two oxygens (μ-O) at 2.01 Å; three oxygens (H$_2$O molecules) at 2.17 Å; two niobium atoms at 2.75 Å and the single capping chlorine atom at 2.49 Å, errors ±0.03 Å, Table 2. Significantly smaller Debye–Waller factors were found, increasing steadily with distance of backscatterer from the absorbing atom, consistent with the more well defined co-ordination sphere around each niobium atom in the now fully aquated cluster.

The fitted distances for the $Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3^{4+}$ core are found to be in excellent agreement with those for the structurally analogous μ$_3$-sulfur-capped $Nb_3(\mu_3\text{-}S)(\mu\text{-}O)_3^{4+}$ core present in the crystal structure of the complex, $[Nb_3(\mu_3\text{-}S)(\mu\text{-}O)_3(NCS)_9]^{6-}$,[3] shown in Table 2 for comparison. Similarly the Nb–Cl distance to the single capping chlorine atom evaluated here (2.49 Å) is in excellent agreement with that found in the

Table 2 Comparison of Nb K edge EXAFS data from the green niobium aqueous cation (0.01 mol dm^{-3} per Nb$_3$) in 3.0 mol dm^{-3} CF$_3$SO$_3$H with crystal structure data on [Nb$_3$(μ$_3$-X)(μ-Y)$_3$L$_9$] species

Species	Nb–O(μ)/Å	Nb–X(μ$_3$)/Å	Nb–Nb/Å	Nb–L/Å	Nb–O–Nb/°
Green niobium aqueous cation {[Nb$_3$(μ$_3$-Cl)(μ-O)$_3$(OH$_2$)$_9$]$^{4+}$}:					
Refined EXAFS data (*ca.* ±0.03 Å)	2.01	2.49(Cl)	2.75	2.17	87(1)*
Refined occupation number (*N*)	2.1	1.0	1.9	2.9	
Debye–Waller factors (2σ^2)	0.001	0.003	0.004	0.002	
AFAC = 0.78; *R* (%) = 34.8387; *FI* = 0.000 66.					
Crystal structural data on [Nb$_3$(μ$_3$-X)(μ-Y)$_3$L$_9$] species:					
[Nb$_3$(μ$_3$-S)(μ-O)$_3$(NCS)$_9$]$^{6-}$ [3]	2.03	2.51(S)	2.76	2.14(N)	86(1)
[Nb$_3$(μ$_3$-Cl)(μ-Cl)$_3$Cl$_6$(PEt$_3$)$_3$]$^{-}$ [11]	—	2.51(Cl)	2.97		
[Nb$_3$(μ$_3$-Cl)(μ-Cl)$_3$Cl$_3$(PEt$_2$Ph)$_6$]$^{-}$ [11]	—	2.47(Cl)	2.83		

* Calculated value.

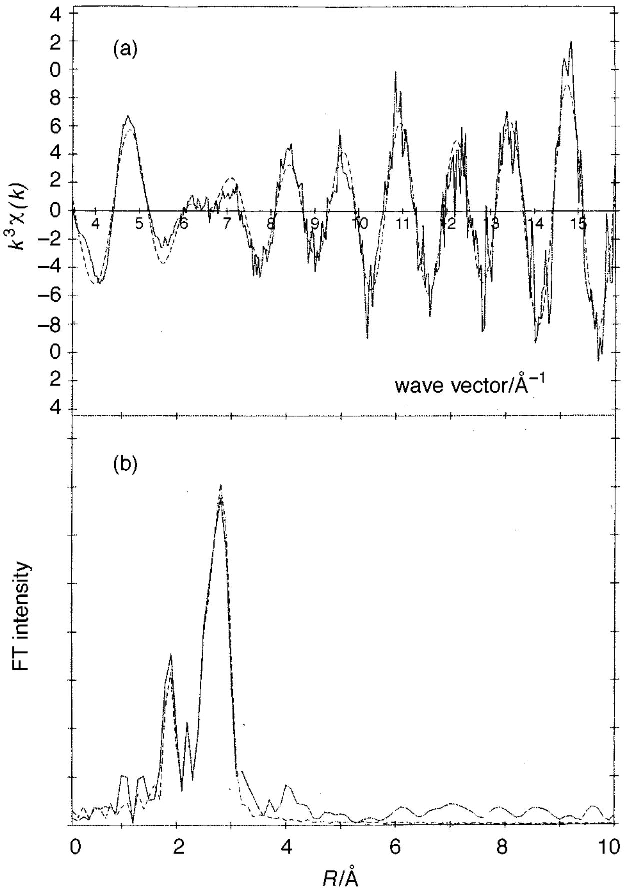
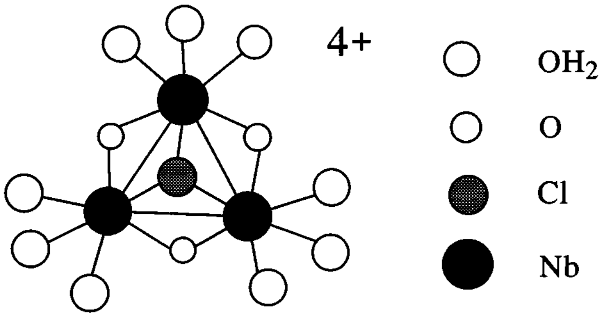


Fig. 2 Experimental (——) and calculated (-----) Nb K edge EXAFS spectrum (a) and Fourier transformed data (b) from the green niobium aqueous cation (0.01 mol dm^{-3} per Nb$_3$) in 3.0 mol dm^{-3} CF$_3$SO$_3$H

crystal structures of two other known μ$_3$-Cl capped triangular niobium cluster complexes, [Nb$_3$(μ$_3$-Cl)(μ-Cl)$_3$Cl$_6$(PEt$_3$)$_3$]$^-$ (2.51 Å)[12] and [Nb$_3$(μ$_3$-Cl)(μ-Cl)$_3$Cl$_3$(PEt$_2$Ph)$_6$]$^-$ (2.47 Å).[12] This excellent agreement in bond distance parameters provides a powerful vindication of the choice of calculated phase shifts.

In conclusion, the success in extracting highly reliable structural parameters for the well characterised [Mo$_3$(μ$_3$-S)(μ-O)$_3$(OH$_2$)$_9$]$^{4+}$ ion, following fits to the refined metal K edge EXAFS pattern obtained from solutions of the above ion,[5] has allowed meaningful evaluation of Nb K edge EXAFS data taken correspondingly from solutions of the green niobium cation. Fits to the latter EXAFS data, along with comparisons from known structural data on several triangular niobium complexes, provides compelling evidence that the green aqueous solutions obtained following acid hydrolysis of trivalent chloroniobium complexes,[1–3] or *via* zinc reduction of NbCl$_5$ in ethanolic HCl,[4] contain the chlorine-capped incomplete cuboidal mixed valence cluster [Nb$_3$(μ$_3$-Cl)(μ-O)$_3$(OH$_2$)$_9$]$^{4+}$ **1**.



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