Characterisation of the Tin(II) Hydroxide Cation $[Sn_3(OH)_4]^{2+}$, and the Crystal Structure of Tritin(II) Tetrahydroxide Dinitrate†

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The crystal structure of $Sn_3(OH)_4(NO_3)_2$ has been determined using single-crystal X-ray diffraction and refined by full-matrix least-squares analysis to $R_1 = 0.0323$ and $wR_2 = 0.1203$. The complex crystallises in the monoclinic space group $P2_1/n$, with $a = 7.729(1)$, $b = 9.086(3)$, $c = 14.159(3)$ Å, $\beta = 90.65(2)°$ and $Z = 4$. The tin(II) atoms are contained in discrete polynuclear $[Sn_3(OH)_4]^{2+}$ cluster units in which each tin is bonded pyramidally to three short nearest-neighbour cluster hydroxide oxygen atoms. A distorted octahedron of oxygen atoms around the tin(II) atoms is completed by three longer contacts to nitrate oxygens in the directions in which the tin non-bonding electron pairs point. One of the OH groups in $[Sn_3(OH)_4]^{2+}$ is unique in that it is bonded to all three cluster tin atoms. This cation is considered to be one of the main products of the hydrolysis of tin(II) in aqueous solution. Raman spectroscopic data for $Sn_3(OH)_4(NO_3)_2$ have also been obtained and the known Mössbauer data are discussed with reference to the structure.

The hydrolysis of tin(II) in aqueous solution has been studied by potentiometric methods[1] which showed that the tin(II) hydroxide species present prior to basic salt precipitation are $[Sn(OH)]^+$, $[Sn_2(OH)_2]^{2+}$ and $[Sn_3(OH)_4]^{2+}$. The polynuclear cation $[Sn_3(OH)_4]^{2+}$ is considered[2] to be the predominant species in the pH range prior to the precipitation of basic tin(II) salts, which should therefore be derivatives of this or a closely related species. The basic tin(II) sulfate,[3,4] $Sn_3O(OH)_2SO_4$, is, for example, a derivative of $[Sn_3O(OH)_2]^{2+}$ which is reported to be formed from $[Sn_3(OH)_4]^{2+}$ by the elimination of one molecule of water at the point of precipitation. The species present in phosphate-containing solutions that gives rise to the basic phosphate, $Sn_3O(OH)PO_4$, may also be related to the predominant cation.[5] There are, however, no reports on the determination of the structure of the $[Sn_3(OH)_4]^{2+}$ ion from which the other basic tin(II) species are likely to be derived. As the pH is raised in a basic salt, such as $Sn_3O(OH)_2SO_4$, the sulfate is gradually replaced by hydroxide ion to give a range of compounds of composition $Sn_3O(OH)_{2+2x}(SO_4)_{1-x}$ which finally dissolves as the $[Sn(OH)_3]^-$ ion at high pH.[6] Donaldson and Moser[7] prepared an explosive crystalline basic tin(II) nitrate, formulated as $Sn_3(OH)_4(NO_3)_2$, which it was suggested contained the $[Sn_3(OH)_4]^{2+}$ ion. The ^{119}Sn Mössbauer data for the compound have also been reported.[6] We now describe the crystal structure of $Sn_3(OH)_4(NO_3)_2$ and interpret the crystallographic data along with Raman spectroscopic and ^{119}Sn Mössbauer data in terms of the chemistry of tin in its 2+ oxidation state.[2,8-10]

Experimental

Preparation.—The synthesis was carried out in an atmosphere of oxygen-free nitrogen using previously degassed solutions. Analytical-grade copper(II) sulfate pentahydrate ($\approx$ 50 g) was dissolved in distilled water (400 cm^3) and concentrated sulfuric acid (20 cm^3). The solution was boiled with analytical-grade metallic tin (50 g) until the solution became colourless and the deposited copper was covered with a grey coating of tin. The resultant solution was filtered and treated with an ammonia (*d* 0.880 Mg m^{-3})–water solution (1 : 1, 280 cm^3) to precipitate hydrous tin(II) oxide. The precipitate was repeatedly centrifuged with successive portions of distilled water until no odour of ammonia was detectable. The resultant paste was filtered under vacuum and partially dried. A solution of analytical-grade nitric acid (*d* 1.42 Mg m^{-3}, 13 cm^3) and distilled water (19 cm^3) was cooled in an ice–salt bath. The hydrous tin(II) oxide paste was added to the nitric acid solution gradually in small portions, with stirring, until the solution was saturated. The temperature was allowed to rise slowly to ambient, progressively saturating the solution with more hydrous tin(II) oxide. The temperature was raised and the procedure repeated until a boiling saturated suspension was attained. The suspension was boiled for 2 min, filtered into a warm, insulated flask and allowed to cool slowly. The crystalline product was filtered off, washed with two small portions of ice-cold ethanol and dried in a vacuum desiccator over KOH pellets. Analysis of the product for tin and nitrate gave 64.7 (64.95) and 22.3% (22.60) respectively, consistent with the formula $Sn_3(OH)_4(NO_3)_2$.

Vibrational Spectra.—Spectra from single crystal samples were recorded on a Renishaw Raman imaging microscope using the 633 nm He–Ne line for excitation. The laser power at the surface of the sample was 8 mW. The scattering volume was approximately 2 μm^3 and spectra were collected in the range 100–4000 cm^{-1} with a spectral resolution of 2 cm^{-1}. The data were collected ten times with an exposure time of 23.44 seconds per scan. Further instrumentation details may be obtained from ref. 11. Raman spectra for a bulk powder sample were collected in the range 200–3000 cm^{-1} using a Perkin-Elmer 1760X FT-Raman spectrometer with a liquid nitrogen cooled detector. The spectra of the bulk powder sample are identical to those of the single crystals used in the X-ray diffraction study. Fig. 1 shows the low- and high-gain Raman spectra for $Sn_3(OH)_4(NO_3)_2$ and the Raman data in the range 200–2000 cm^{-1} are presented in Table 4.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Crystallography.—*Crystal data*. $H_4N_2O_{10}Sn_3$, $M = 548.11$, monoclinic, space group $P2_1/n$, $a = 7.729(1)$, $b = 9.086(3)$, $c = 14.159(3)$ Å, $\beta = 90.65(2)°$, $U = 994.26$ Å^3, $T = 298$ K, $Z = 4$, $D_c = 3.662$ g cm^{-3}, colourless crystals, crystal size 0.4 × 0.2 × 0.1 mm, $F(000) = 992$, μ(Mo-Kα) = 7.52 cm^{-1}.

Data collection and processing. Intensity data were collected on an Enraf-Nonius CAD4 four-circle diffractometer in the ω–2θ scan mode. Monochromatic Mo-Kα ($\lambda = 0.710\,69$ Å) radiation was used throughout. 2456 Reflections were measured between 2.66 and 26.98°, of which 2162 were unique in monoclinic symmetry (merging R factor 0.014). An empirical absorption correction was applied ($T_{min} = 0.7576$, $T_{max} = 0.9971$).

Structure analysis and refinement. The systematic absences in the intensity data confirmed the space group as $P2_1/n$ (no. 14). Using this space group the three tin and four oxygen atoms associated with the $[Sn_3(OH)_4]^{2+}$ unit were located by direct methods using SHELX 86.[12] These atom positions were refined using SHELX 76[13] from which a Fourier-difference map was generated enabling the location of the remaining nitrate and hydrogen atoms. Anisotropic thermal parameters were applied to all non-hydrogen atoms. Constraints were applied to the hydrogen atoms to fix the bond length to the associated oxygen atoms within the metal hydroxide cluster at 0.96(2) Å.

The final refinement was undertaken using SHELX 93[14] for all 2162 reflections. Non-unitary weights were used, the weighting scheme being $w = 1/[\sigma^2(F_o^2) + (0.1000P)^2 + 0.00P]$ where $P = [\max(F_o^2, 0) + 2F_c^2]/3$. Refinement was terminated with $R_1 = 0.0323$ for 1857 reflections where $F_o > 4\sigma(F_o)$, and $R_1 = 0.0408$ ($wR_2 = 0.1203$) for all 2162 reflections. The maximum residual electron density in the final refinement was 1.47 e Å^{-3} and was associated with residual density from the tin atoms. An average shift : e.s.d. of 0.016 for all parameters was obtained in the final refinement. The final atomic parameters are given in Table 1, with selected contact distances and bond angles given in Table 2.

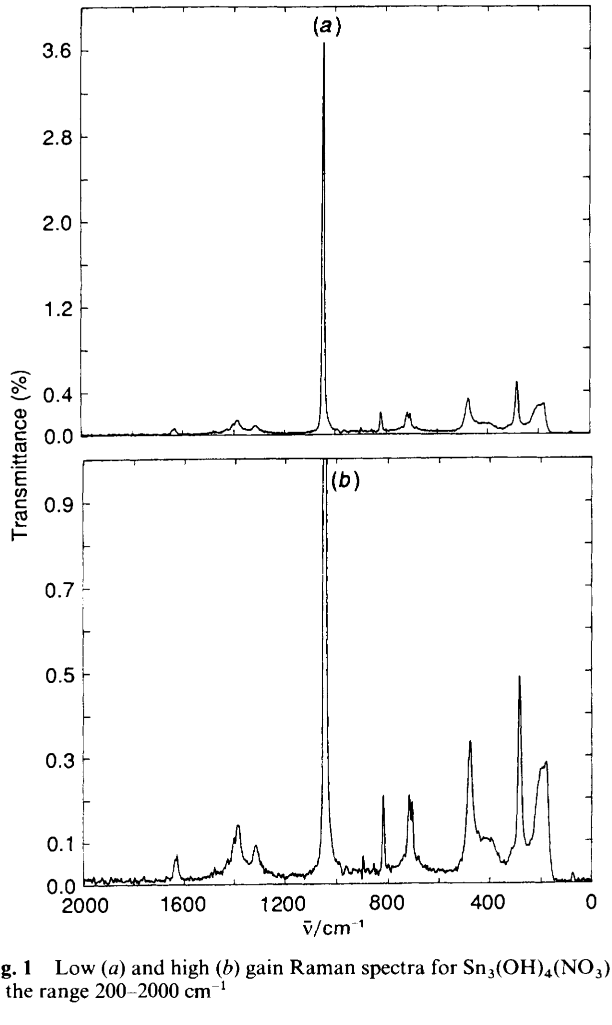

Fig. 1 Low (*a*) and high (*b*) gain Raman spectra for $Sn_3(OH)_4(NO_3)_2$ in the range 200–2000 cm^{-1}

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Discussion

A projection of the unit-cell contents for $[Sn_3(OH)_4][NO_3]_2$ is shown in Fig. 2. The structure consists of distinct $[Sn_3(OH)_4]^{2+}$ groups with nitrate ions present as the counter ions occupying the regions between the clusters. The asymmetric unit consists of one $[Sn_3(OH)_4]^{2+}$ cluster and two nitrate ions. The arrangement of atoms in the $[Sn_3(OH)_4]^{2+}$ group is shown in Fig. 3. The clusters consist of three approximately equidistant tin(II) atoms in a plane with three of the hydroxide groups on one side of the plane and one hydroxide group on the other. The four hydroxide oxygen atoms form a slightly distorted tetrahedron with the tin atoms positioned outside three of the faces of the tetrahedron. There are, therefore, two types of hydroxide oxygen environment in

Table 1 Fractional atomic coordinates for $[Sn_3(OH)_4][NO_3]_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Sn(1)	0.035 52(6)	0.197 80(6)	0.178 44(3)
Sn(2)	−0.213 60(7)	0.222 50(6)	0.388 32(3)
Sn(3)	−0.416 00(6)	0.236 19(6)	0.161 55(4)
O(1)	−0.400 4(6)	0.119 5(5)	0.295 7(3)
O(2)	−0.196 6(6)	0.329 9(5)	0.241 7(3)
O(3)	−0.033 3(6)	0.094 0(6)	0.309 8(3)
O(4)	−0.201 0(6)	0.101 8(5)	0.126 3(3)
N(1)	−0.181 8(8)	0.410 9(6)	0.975 3(4)
O(11)	−0.049 2(7)	0.343 4(8)	0.998 7(4)
O(12)	−0.204 3(7)	0.447 3(7)	0.891 3(4)
O(13)	−0.293 3(8)	0.443 3(6)	1.035 7(4)
N(2)	−0.227 2(9)	0.570 7(7)	0.614 0(4)
O(21)	−0.113(1)	0.632(1)	0.569 9(5)
O(22)	−0.357(1)	0.529(1)	0.570 4(7)
O(23)	−0.215(2)	0.550(1)	0.697 8(5)
H(1)	−0.482(13)	0.069(13)	0.333(8)
H(2)	−0.190(10)	0.434(2)	0.238(5)
H(3)	0.067(5)	0.083(7)	0.349(3)
H(4)	−0.165(18)	0.064(17)	0.067(5)

Table 2 Selected bond distances (Å) and angles (°) within a $[Sn_3(OH)_4]^{2+}$ cluster with e.s.d.s in parentheses

Sn(1)–Sn(2)	3.5663(10)	Sn(3)–O(4)	2.126(5)
Sn(1)–Sn(3)	3.5126(8)	O(1)–O(2)	2.599(7)
Sn(2)–Sn(3)	3.5578(11)	O(1)–O(3)	2.852(7)
Sn(1)–O(2)	2.345(5)	O(1)–O(4)	2.870(7)
Sn(1)–O(3)	2.158(5)	O(2)–O(3)	2.662(7)
Sn(1)–O(4)	2.149(5)	O(2)–O(4)	2.639(7)
Sn(2)–O(1)	2.153(5)	O(3)–O(4)	2.891(7)
Sn(2)–O(2)	2.299(5)	H(1)–O(1)	0.95(11)
Sn(2)–O(3)	2.138(5)	H(2)–O(2)	0.95(2)
Sn(3)–O(1)	2.178(5)	H(3)–O(3)	0.95(10)
Sn(3)–O(2)	2.201(5)	H(4)–O(4)	0.95(4)
Sn(2)–Sn(1)–Sn(3)	60.34(2)	O(1)–Sn(3)–O(2)	72.79(2)
Sn(3)–Sn(2)–Sn(1)	59.08(2)	O(1)–Sn(3)–O(4)	83.65(2)
Sn(2)–Sn(3)–Sn(1)	60.58(2)	O(2)–Sn(3)–O(4)	75.13(2)
O(2)–Sn(1)–O(4)	71.77(2)	Sn(2)–O(1)–Sn(3)	110.44(2)
O(2)–Sn(1)–O(3)	72.36(2)	Sn(2)–O(2)–Sn(3)	104.46(2)
O(3)–Sn(1)–O(4)	84.35(2)	Sn(1)–O(2)–Sn(2)	100.34(2)
O(1)–Sn(2)–O(2)	71.32(2)	Sn(1)–O(2)–Sn(3)	101.15(2)
O(1)–Sn(2)–O(3)	83.27(2)	Sn(2)–O(3)–Sn(1)	112.21(2)
O(2)–Sn(2)–O(3)	73.64(2)	Sn(1)–O(4)–Sn(3)	110.53(2)

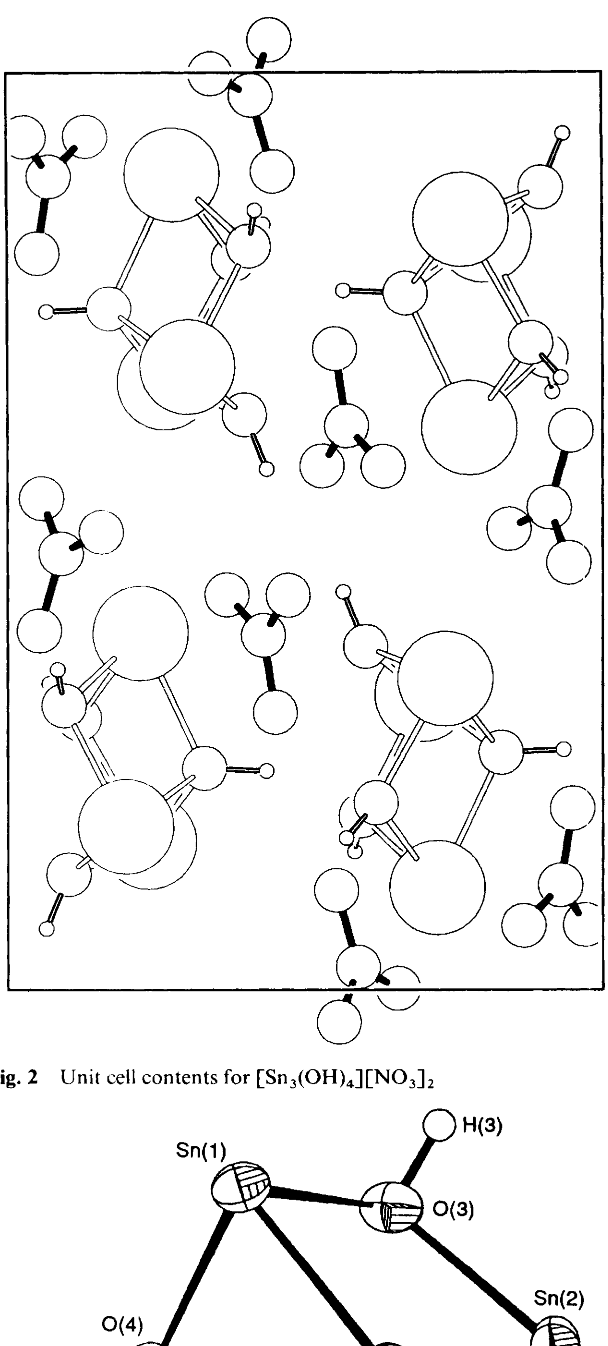

Fig. 2 Unit cell contents for $[Sn_3(OH)_4][NO_3]_2$

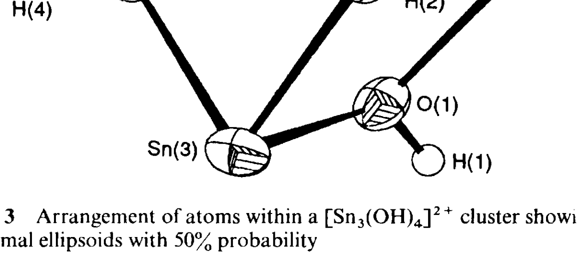

Fig. 3 Arrangement of atoms within a $[Sn_3(OH)_4]^{2+}$ cluster showing thermal ellipsoids with 50% probability

the $[Sn_3(OH)_4]^{2+}$ cluster. One hydroxide group OH(2) is unusual in that it is located between three nearest-neighbour tin atoms and is not equidistant from all three Sn atoms but is significantly closer to one tin atom [Sn(3)]. The remaining three hydroxide groups have only two nearest neighbour tin atoms. These differences are reflected in the oxygen–oxygen distances within the cluster. The average O···O distance involving OH(2) is 2.633(7) Å while the average O···O distances between the remaining three hydroxide groups is 0.24 Å longer at 2.871(7) Å. The hydrogen atoms in the $[Sn_3(OH)_4]^{2+}$ cluster, which point away from the centre of the group, were fixed at 0.96(2) Å from the O atoms. The two nitrate groups present in the asymmetric unit have an average N–O bond distance of 1.232(9) Å and an average O–N–O bond angle of 120.0(7)°. All of the hydrogen atoms in the $[Sn_3(OH)_4]^{2+}$ cluster are less than 2.0 Å from the oxygen atoms of neighbouring groups within the cell. In the case of the three OH groups bonded to two tin atoms, the hydrogen atoms are close to nitrate O atoms. Although the hydrogen atom from hydroxide group OH(2) lies approximately 3 Å away from the nearest nitrate oxygen, it is only 1.88 Å from a hydroxide oxygen atom [OH(1)] from an adjacent $[Sn_3(OH)_4]^{2+}$ cluster. The O···O van der Waals distance, in the absence of hydrogen bonding, should be 2.80 Å so that the shortening of all of these contacts in the neighbourhood of the $[Sn_3(OH)_4]^{2+}$ clusters is indicative of significant hydrogen-bonding interactions. Although the $[Sn_3(OH)_4]^{2+}$ ions in the lattice are discrete, the structure is held together by the hydrogen-bonding network in addition to the electrostatic cluster-cation–nitrate-anion interactions. The immediate tin(II) environment of all of the Sn atoms in $[Sn_3(OH)_4][NO_3]_2$ is a distorted trigonal-pyramidal arrangement of three nearest-neighbour tin–oxygen bonds. Each Sn atom has bonds to the two different types of OH group in the cluster *viz.* one bond to the hydroxide OH(2) (2.20–2.35 Å) and two bonds to two of the other hydroxides (2.13–2.18 Å). These differences in Sn–O bond lengths are consistent with OH(2) bridging all three Sn atoms while the other hydroxides bridge only two Sn atoms. The average O–Sn–O bond angles are 72.84(18)° for angles involving OH(2) and 83.76(18)° for the bond angles involving the other cluster hydroxides. Although the O–Sn–O angles are typical[15] of those found in tin(II) oxygen-containing compounds they, and particularly the angles involving OH(2), are constrained by the cluster formation requirements. Tin(II) atoms with pyramidal three-co-ordinated environments are present in a large number of tin(II) compounds.[2,8–10] In this type of arrangement the tin atom typically has three short bonds and three longer distances to other ligands that complete a distorted-octahedral arrangement. In $[Sn_3(OH)_4][NO_3]_2$, each tin atom has, in addition to the three short Sn–O bonds, three nitrate oxygen atoms at longer distances completing the distorted octahedron. These longer contacts are in the ranges 2.70–2.94, 2.75–3.10 and 2.77–3.52 Å for Sn(1), Sn(2) and Sn(3) respectively. The distorted-octahedral arrangement arises because of the need to accommodate the non-bonding electron pair on the tin(II) atoms. The directional non-bonding electron pair points along the approximately three-fold axis of the pyramid of three short Sn–O bonds and prevents the close approach of oxygen atoms along the direction in which it points giving rise to the three longer Sn–O contacts.

The average tin–tin distance in the $[Sn_3(OH)_4]^{2+}$ cluster is 3.5456(10) Å. Although this distance could arise from the constraints of the cluster, it is short enough to consider the possible presence of tin–tin bonding interactions. The shortest inter-metallic Sn–Sn distances in α-tin and β-tin are 2.80 and 3.07 Å respectively and, therefore, any distance which is less than 4 Å could be regarded as involving some form of interaction between the tin atoms. The ability of tin, in its 2+ oxidation state, to achieve short Sn–Sn distances by metal–metal bonding interactions and by bridging structure constraints is well illustrated by the structure of blue-black tetragonal tin(II) oxide.[15] In tin(II) oxide, which has a layer structure, tin–tin interlayer interactions result in the delocalisation of the non-bonding pair of electrons into adjacent layer solid-state tin bands giving Sn–Sn distances of 3.70 Å. These Sn–Sn bonding interactions are responsible for the relatively high four-fold symmetry of the tin–oxygen environment and for the optical and other properties of the material.[9,10] This interaction does

Table 3 Tin-119 Mössbauer chemical shift parameters and Sn–O bond lengths for some tin compounds

Compound	Average Sn–O bond length/Å	Shift/mm s^{-1}
$Sn_3(OH)_4(NO_3)_2$		
Sn(1)	2.22	
Sn(2)	2.20	3.73
Sn(3)	2.17	
$K_3Sn_2(SO_4)_3Br$	2.55	3.86
$SnSO_4$	2.26	3.95
$SnHPO_3$	2.17	3.15
$KSn(O_2CH)_3$	2.16	3.08
$CaSn(O_2CMe)_3$	2.14	2.90

Table 4 Raman spectrum of $Sn_3(OH)_4(NO_3)_2$ in the range 200–2000 cm^{-1}

Observed data/cm^{-1}	Relative peak intensity	Assignment of vibrations
203	7	$[Sn_3(OH)_4]^{2+}$
283	14	$[Sn_3(OH)_4]^{2+}$
403	2	$[Sn_3(OH)_4]^{2+}$
464	10	$[Sn_3(OH)_4]^{2+}$
705	5	NO_3^-
718	6	NO_3^-
820	6	NO_3^-
1045	100	NO_3^-
1314	3	NO_3^-
1386	4	NO_3^-
1629	2	NO_3^-
1637	2	NO_3^-

not, however, result in the shortest tin–tin distance in SnO. The shortest distance (3.51 Å) is between adjacent intralayer tin atoms that are bridged by oxygens in square-pyramidal co-ordination. The presence of short inter- and intra-layer distances in SnO illustrates the fact that short tin–tin distances can arise either by constraints imposed by bridging effects (intralayer) or by tin–tin bonding interactions involving the tin(II) non-bonding electron pairs (interlayer). Since the non-bonding electron pair orbitals on the tin atoms in the $[Sn_3(OH)_4]^{2+}$ cluster point outwards from the cluster they cannot take part in tin–tin bonding interactions and, for this reason, the short Sn–Sn distances in the cluster must arise because of the constraints of the cluster bridging situation. This is in contrast to the situation in compounds such as $K_3Sn_2(SO_4)_3Br$ where non-bonding electron pairs point towards the centre of an octahedral cluster and populate cluster orbitals.[16] The Sn $\cdots$ Sn distances between adjacent $[Sn_3(OH)_4]^{2+}$ clusters are greater than 4.25 Å and this precludes any inter-cluster tin–tin interactions.

The three tin sites in $Sn_3(OH)_4(NO_3)_2$ are similar and the ^{119}Sn Mössbauer spectrum (δ = 3.48 mm s^{-1} from $BaSnO_3$, Δ = 1.85 mm s^{-1}) consists of three unresolved overlapping sub-spectra that represent the average use of Sn outer electrons in bonding. We have previously studied the relationship between ^{119}Sn Mössbauer chemical shift parameters and bond lengths and found, for example,[2] that for a number of tin(II) compounds with Sn–L (L = F, Cl, O or S) bonds to the same type of ligand atom there is a close relationship between the Mössbauer chemical shift and the average Sn–L bond distances; *viz.*, an increase in average bond length results in an increase in shift. The data for $Sn_3(OH)_4(NO_3)_2$ in Table 3 show that the relationship between the shift and bond distances in the trigonal-pyramidal co-ordination of tin atoms holds for this basic salt.

The Raman spectroscopic data for $Sn_3(OH)_4(NO_3)_2$ are recorded in Table 4. No previous Raman spectra have been reported for $Sn_3(OH)_4(NO_3)_2$ or for any solids or solutions containing the $[Sn_3(OH)_4]^{2+}$ cluster. Apart from a broad low intensity peak at 3000–3200 cm^{-1} which corresponds to the OH stretching modes, all of the frequencies recorded above 700 cm^{-1} are closely correlated to those of the nitrate ion[17] differentiating them from frequencies resulting from the $[Sn_3(OH)_4]^{2+}$ moiety at 203, 283, 403 and 464 cm^{-1}. The presence of the nitrate band at 820 cm^{-1} which would be Raman inactive for an ion with D_{3h} symmetry is consistent with a reduction in the symmetry of the NO_3^- group because of differing nitrate–oxygen interactions with the $[Sn_3(OH)_4]^{2+}$ cluster. Factor group analysis for the Sn_3O_4 cage, assuming C_{3v} symmetry, predicts a total of 12 Raman-active vibrational modes only four of which are observed presumably because of a combination of overlapping frequencies, low-intensity vibrations and frequencies below 100 cm^{-1}.

It has been suggested that the cationic cluster $[Sn_3O(OH)_2]^{2+}$ found in the basic tin(II) sulfate $Sn_3O(OH)_2SO_4$ could be derived from $[Sn_3(OH)_4]^{2+}$ by loss of one molecule of water. Because of the fact that OH(2) is unique in $[Sn_3(OH)_4]^{2+}$ in that it is bonded to all three tin atoms and because it is nearer to OH(1) (2.60 Å) than to the other hydroxides, it seems likely that loss of water would occur from these OH groups. The resulting $[Sn_3O(OH)_2]^{2+}$ ion would not have sufficient oxygen donors to form the typical pyramidal three co-ordination to the tin(II) and this is reflected in the use of sulfate oxygen atoms to complete the Sn co-ordination in the basic sulfate. The environments of the tin(II) atoms in $Sn_3(OH)_4(NO_3)_2$ are consistent with the theoretical descriptions of the bonding of main-group elements in their low-oxidation states in situations where the non-bonding electron pairs have high p character and are directional and in which there are no solid-state interactions.[9,10]

Acknowledgements

We thank the SERC for an award to S. R. J. We also thank M. Motevalli at Queen Mary and Westfield College, London for data collection, Professor D. N. Batchelder at Leeds University for the use of a Raman imaging microscope and Dr. D. N. Waters at Brunel University for collection of bulk Raman spectroscopic data.

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Received 24*th November* 1994; *Paper* 4/07173E