Synthesis and Crystal Structure of a New Oxo Perchlorato Complex of Tin(IV): $[Sn_3O_2Cl_4(ClO_4)_4]_2$

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Summary *X*-Ray diffraction, i r , and Raman spectroscopic studies of the new compound $[Sn_3O_2Cl_4(ClO_4)_4]_2$ provide evidence for bidentate and unidentate perchlorato groups strongly co-ordinated to the Sn atoms

Using the classical reaction of Cl_2O_6 with metallic chlorides which has been developed during the past few years,[1,2] we have prepared $(ClO_2)_2Sn(ClO_4)_6$ from $SnCl_4$ at 10 °C This red and very hygroscopic solid, first discovered by Schmeisser *et al* ,[1] reacts with an excess of $SnCl_4$ at 10 °C to give a colourless solid identified as $Sn_3O_2Cl_4(ClO_4)_4$ Single hygroscopic crystals of the latter can be obtained from the saturated solution by cooling to −20 °C and these were handled in dry fluorocarbon oil in a dry box

Crystal data $Sn_3O_2Cl_4(ClO_4)_4$, $M = 927{\cdot}7$, orthorhombic space group, *Pccn*, $a = 10{\cdot}251$, $b = 16{\cdot}429$, $c = 24\ 659$ Å, $Z = 8$, $D = 2{\cdot}98$ g cm^{-3}, μ (Mo-K_α) = 47 cm^{-1} Intensity data were collected by the ω–2θ scan technique on a Nonius CAD 4 diffractometer ($0 \leqslant 2\theta \leqslant 25°$), 1367 unique reflexions with $I > 3\sigma(I)$ were obtained The structure was solved by direct methods and refined to a current *R* of 9% with anisotropic temperature factors for Sn and Cl and isotropic temperature factors for O †

Two asymmetric units $Sn_3O_2Cl_2(ClO_4)_2$ are related by a centre of symmetry giving a dimeric $Sn_6O_4Cl_8(ClO_4)_8$

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† The atomic co-ordinates for this work are available on request from Prof Dr G Bergerhoff, Institut fur Anorganische Chemie, Universitat, Gerhard-Domagk-Str 1, D-5300 Bonn 1, West Germany Any request should be accompanied by the full literature citation for this communication

conformation. A schematic drawing of the structure is given in the Figure.

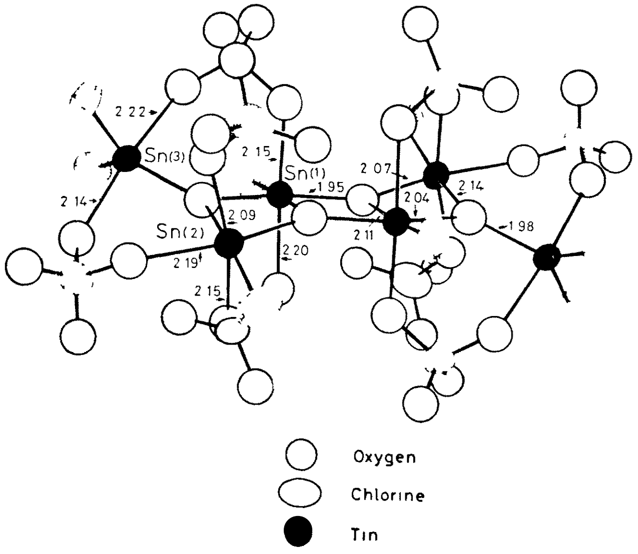

FIGURE. The dimeric molecule $[Sn_3O_2Cl_4(ClO_4)_4]_2$. Average standard deviation for Sn–O bond lengths = 0·03 Å.

This structure is built on an Sn_6O_4 model of the rutile type with planar trico-ordinated oxygen atoms, analogous to the cassiterite structure. Internal cohesion of the model is ensured by six bridging bidentate ClO_4 groups. Two other ClO_4 unidentate groups and eight chlorine atoms ensure electroneutrality of the molecule. Sn(3) and Sn(3′) are 5-co-ordinate; Sn(1), Sn(1′), Sn(2), and Sn(2′) are 6-co-ordinate. The short distances Sn(1′)–Sn(1) and Sn(1)–Sn(2) [3·24(1) Å] may indicate metal–metal interactions (primes refer to the transformation with respect to the crystallographic centre within the dimeric units). The perchlorate geometries are poorly determined owing to the high thermal motion of non-co-ordinated oxygen atoms. However this problem of high thermal motion does not lead to any ambiguity with regard to the co-ordination of the perchlorate groups. The average distance between Sn atoms and co-ordinated oxygens of the perchlorate is 2·16(2) Å. This is the first direct evidence of a strongly co-ordinated perchlorate ligand in a totally inorganic material. For comparison a distance of 2·91(1) Å between tin and perchlorate oxygen atoms has been observed in $[Cl_3SnOClO_3]^-$[3] but a distance of 2·30 Å has been found already in a perchlorato manganese complex with a macrocyclic ligand.[4] Recently a very short metal–oxygen distance of 2·03 Å has been reported for a perchlorato ferric porphyrin.[5]

I.r. and Raman spectra were consistent with the occurrence of both unidentate and bidentate perchlorato groups; *cf.* previous work on perchlorato compounds:[2,6] i.r., unidentate groups, ν_{as} (ClO_f) 1245, ν_s (ClO_f) 1025, and ν_s (ClO_b) 745 cm^{-1} (O_f free terminal oxygen, O_b oxygen bonded to Sn); bidentate groups ν_{as} (ClO_f) 1275, ν_s (ClO_f) 1145, and ν_s and ν_{as} ClO_b 900—860 cm^{-1}. Sn–O_b stretching modes are located at 325—295 cm^{-1}. Symmetric and asymmetric stretching modes of Sn–O–Sn bridges are assigned at *ca.* 420 and 730 cm^{-1} in agreement with similar assignments in the Me_6Sn_2O spectrum.[7]

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