Derivatives of Bivalent Germanium, Tin, and Lead. Part XVIII.[1] Crystal and Molecular Structure, and Variable-temperature Mössbauer Effect of Octakis-μ-(*o*-nitrobenzoato)-di-μ_3-oxo-bis(tetrahydrofuran)ditin(II)-ditin(IV)

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The crystal and molecular structure of the title compound has been determined by Patterson and Fourier methods from diffractometer data to a final *R* value of 0.062 for 5 146 independent, non-zero reflections. Crystals are monoclinic, space group $P2_1/c$, a = 13.426(4), b = 14.666(3), c = 22.029(5) Å, β = 115.51(2)°, Z = 2. The structure consists of independent tetranuclear cluster molecules containing two tin(II) and two tin(IV) atoms. The central feature of the macromolecule is a lozenge-shaped four-membered $Sn^{IV}{}_2O_2$ ring. Octahedral co-ordination at each tin(IV) atom is completed by oxygen atoms from four *o*-nitrobenzoate groups [r(Sn^{IV}–O) 2.047(6)—2.067(7) Å], which form bridges between the tin atoms in each valence state. The geometry at the bivalent tin atoms is that of a distorted pentagonal pyramid with oxygen atoms from four bridging carboxylate groups and tetrahydrofuran occupying equatorial positions at bond distances in the range 2.409(8)—2.661(9) Å. The apical site of the pentagonal pyramid is occupied by the oxygen atom of the four-membered Sn_2O_2 ring at the extremely short tin(II)–oxygen distance of 2.113(7) Å. The tin(II) lone-pair electrons are presumably in the remaining apical position. The partial oxidation of tin(II), which takes place in the synthesis of the compound, is deduced to take place by interaction with the *o*-nitrobenzoate groups. From the variable-temperature Mössbauer effect, the Debye temperatures for the tin(II) and tin(IV) atoms were determined to be 104.1 and 119.6 K.

FEW mixed-valence derivatives of the heavier Group IV elements have been characterised. The structures of two mixed-valence binary fluorides, Ge_5F_{12} and Sn_3F_8, have been determined.[2,3] Both contain $M^{IV}F_6$ units in infinite arrays. The mixed-valence oxide of lead, Pb_3O_4, is well known, and contains an octahedrally co-ordinated Pb^{IV} atom together with a Pb^{II} atom at the apex of a trigonal pyramid of oxygen atoms.[4] More recently, the mixed-valence oxide of tin, Sn_2O_3, has been prepared, and its Mössbauer spectrum interpreted in terms of similar octahedral and pyramidal co-ordination of Sn^{IV} and Sn^{II}, respectively.[5,6] The mixed-valence sulphide, Sn_2S_3, has the same structure.[7,8] Mössbauer spectroscopy has also been used to demonstrate the presence of both valence states in the partially-oxidised ternary oxide systems, $Sn_2Nb_2O_7$ and $Sn_2Ta_2O_7$.[9] The most surprising mixed-valence compound yet reported, however, is nitrato-(triphenylstannio)tin(II), which is obtained by the reaction of diphenyltin(IV) dinitrate and triphenylarsine, a reaction which involves reduction of quadri- to di-valent tin in the presence of the strongly oxidising nitrato-ligand. The tin(II) atoms in the compound are five-co-ordinated by two chelating nitrato-groups and the triphenyltin(IV) residue.[10]

Previously,[11] we have described the formation of an anomalous product from the reaction of bis(methylcyclopentadienyl)tin and two moles of *o*-nitrobenzoic acid in tetrahydrofuran (thf). Since the usual techniques for characterisation were of little use and the Mössbauer spectrum of the crystalline material showed it to contain tin in both its II and IV valence states, an *X*-ray diffraction study was instituted, the results of which are reported here.

EXPERIMENTAL

Crystals of the title compound suitable for intensity measurements crystallised slowly from a thf solution of *o*-nitrobenzoic acid (2 mol) and bis(methylcyclopentadienyl)tin (1 mol) which had been heated under reflux. The crystals could not be redissolved in thf even on heating, and were insoluble in all common organic solvents. The cuboid, pale fawn crystals were air-sensitive but stable to *X*-rays, and a crystal of dimensions *ca.* 0.4 × 0.4 × 0.5 mm was mounted

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[3] M. F. A. Dove, R. King, and T. J. King, *J.C.S. Chem. Comm.*, 1973, 944.

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[5] G. Murken and M. Trömel, *Z. anorg. Chem.*, 1973, **397** 117.

[6] K. Hasselbach, G. Murken, and M. Trömel, *Z. anorg. Chem.*, 1973, **397**, 127.

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[8] S. Ichiba, M. Katada, and H. Negita, *Inorg. Nuclear Chem. Letters*, 1974, 979.

[9] D. J. Stewart, O. Knop, R. E. Meads, and W. G. Parker, *Canad. J. Chem.*, 1973, **51**, 1041.

[10] M. Nardelli, C. Pellizzi, and G. Pellizzi, *J. Organometallic Chem.*, 1974, **85**, C43.

[11] P. F. R. Ewings and P. G. Harrison, *J.C.S. Dalton*, 1975, 1717.

in a Lindemann capillary under nitrogen and used for the determination of initial cell parameters and subsequent intensity data.

Crystal Data.—$C_{64}H_{48}N_8O_{36}Sn_4$, $M = 1\,979.89$, $a = 13.426(4)$, $b = 14.666(3)$, $c = 22.029(5)$ Å, $\beta = 115.51(2)°$, $U = 2\,747.02$ Å^3, $Z = 2$, $F(000) = 1\,952$, μ(Mo-K_α) = 19.99 cm^{-1}. Space group $P2_1/c$ by systematic absences ($0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$). The space group and initial cell parameters were determined from zero- and first-layer Weissenberg photographs obtained by use of a Nonius Weissenberg goniometer. Cell parameters were further refined by least-squares methods from *ca.* 20 reflections. Relative intensities up to $\theta = 30.0°$ were collected by use of Mo-K_α radiation ($\lambda = 0.710\,69$ Å) on a Hilger and Watts Y 290 four-circle diffractometer. Each reflection was counted for 30 s and the two associated background counts for 10 s. The reflections were brought to the same relative intensities by a reference reflection monitored every 100 reflections, the diffractometer being monitored every 200 reflections. The background counts were low and were included in the usual way. Of 4 224 reflections measured, those with a corrected count $I < 3\sigma(I)$ were considered unobserved and were not further used. The remaining 3 264 reflections were further reduced to 2 138 by eliminating those of lowest intensity in order to enable adequate computer storage for solution and initial refinement. Intensities were corrected for Lorentz and polarisation effects, but not for absorption correction because of the low value of μ.

Structure Determination and Refinement—The positional parameters of the two tin atoms in the asymmetric unit were obtained from a three-dimensional Patterson synthesis, and were used to phase the initial structure-factor calculation. Two cycles of isotropic block-diagonal least-squares refinement of these positions followed by a Fourier synthesis revealed 41 possible light-atom positions, and when these were included the same procedure yielded a further six light-atom positions. However, on examination, ten of these were removed because of unsatisfactory thermal parameters. A second structure-factor calculation at this stage showed that R had fallen to 0.16. A difference-Fourier synthesis revealed a further four light atoms in positions which fitted a chemically acceptable model. The positions of the atoms so far located were then refined by isotropic block-diagonal least squares, and subsequently ten light-atom positions with satisfactory thermal parameters were discarded. At this point the two tin atoms were allowed to vary anisotropically, and two cycles of block-diagonal least-squares refinement followed by a difference-Fourier synthesis revealed 14 new light atoms in positions which were chemically acceptable. Four cycles of block-diagonal least-squares refinement followed by a further difference-Fourier synthesis yielded the remaining nine light-atom positions. All atom positions were then refined by six cycles of block-diagonal least squares, giving R 0.069. The inclusion of the 24 hydrogen atoms, whose positions had been previously calculated, did not produce any significant improvement, and these were therefore discarded. Convergence was achieved, after a further six cycles of least-squares refinement, at R 0.062 for 2 138 reflections, the positional and thermal parameters for one of the nitro-groups being held invariant for the final two cycles (see text). At this stage, all 5 146 available reflections were included, and six cycles of isotropic block-diagonal refinement (with the tin atoms varying anisotropically), followed by eight cycles of anisotropic block-diagonal refinement reduced R to 0.059. Because of difficulty experienced in the refinement of the nitro-group positions, the four nitro-groups were blocked so that the atoms in each group refined together. Six cycles of anisotropic refinement with the positional and thermal parameters of N(4), O(27), and O(15) held invariant gave R 0.063. The weighting scheme $w = (A/F_o)^2$, where $A = 100.0$, was then applied, followed by two cycles of anisotropic block-diagonal least squares giving a final R of 0.062. Scattering factors for neutral atoms were taken from ref. 12.

TABLE 1

Final fractional atomic co-ordinates

Atom	x/a	y/b	z/e
Sn(1)	0.625 68(5)	0.007 83(5)	0.028 29(3)
Sn(2)	0.488 94(6)	0.126 80(6)	0.125 13(4)
O(1)	0.633 4(7)	−0.003 5(6)	0.176 3(4)
O(2)	0.627 0(6)	0.390 6(5)	0.463 9(3)
O(3)	0.242 3(5)	0.450 5(5)	0.483 6(3)
O(4)	0.625 1(8)	0.481 2(6)	0.382 9(4)
O(5)	0.355 1(6)	0.407 4(5)	0.402 5(3)
O(6)	0.746 8(6)	0.081 7(6)	0.095 0(4)
O(7)	0.662 9(6)	0.185 3(6)	0.132 6(4)
O(8)	0.305 4(6)	0.158 1(6)	0.057 8(4)
O(9)	0.176 1(11)	0.466 1(8)	0.217 5(7)
O(10)	0.273 1(15)	0.452 6(9)	0.159 2(6)
O(11)	0.780 1(20)	0.417 6(14)	0.141 1(12)
O(12)	0.753 3(23)	0.459 9(11)	0.303 0(15)
O(13)	0.750 5(13)	0.315 3(11)	0.067 5(8)
O(15) *	0.162 8(10)	0.276 1(10)	0.419 1(8)
O(16)	0.471 6(8)	0.275 2(7)	0.073 3(5)
O(18)	0.592 2(29)	0.445 5(11)	0.243 3(9)
O(20)	0.493 6(5)	0.065 3(4)	0.039 5(3)
O(27) *	0.011 0(3)	0.254 3(13)	0.392 1(9)
N(1)	0.669 8(28)	0.418 8(10)	0.284 4(10)
N(2)	0.240 5(13)	0.428 1(9)	0.201 9(6)
N(3)	0.797 1(15)	0.341 5(12)	0.120 0(15)
N(4) *	0.090 8(16)	0.286 1(51)	0.420 7(19)
C(1)	0.455 6(19)	0.357 1(13)	0.005 5(8)
C(2)	0.421 7(30)	0.116 9(15)	0.490 2(12)
C(3)	0.423 7(34)	0.425 0(14)	0.054 9(14)
C(4)	0.447 2(28)	0.357 1(13)	0.098 9(12)
C(10)	0.232 7(8)	0.113 3(8)	0.020 7(5)
C(11)	0.120 9(8)	0.129 2(8)	0.015 9(5)
C(12)	0.090 5(12)	0.092 9(12)	0.062 2(7)
C(13)	0.981 8(12)	0.106 2(13)	0.059 6(8)
C(14)	0.913 1(11)	0.150 7(14)	0.012 4(9)
C(15)	0.939 8(15)	0.315 3(28)	0.465 4(12)
C(16)	0.047 1(14)	0.324 1(19)	0.470 6(9)
C(20)	0.743 9(9)	0.150 0(9)	0.129 4(5)
C(21)	0.848 8(10)	0.188 1(10)	0.169 3(6)
C(22)	0.922 2(11)	0.131 7(15)	0.210 1(7)
C(23)	0.025 6(15)	0.164 0(19)	0.254 0(9)
C(24)	0.044 2(17)	0.257 2(22)	0.251 6(10)
C(25)	0.970 1(18)	0.318 5(19)	0.211 2(11)
C(26)	0.869 8(12)	0.282 8(13)	0.168 9(7)
C(30)	0.351 5(9)	0.423 2(8)	0.343 9(5)
C(31)	0.332 0(9)	0.339 3(8)	0.302 9(5)
C(32)	0.363 8(10)	0.255 8(9)	0.331 0(7)
C(33)	0.354 5(14)	0.175 6(11)	0.294 0(7)
C(34)	0.311 7(13)	0.182 3(10)	0.226 6(7)
C(35)	0.275 0(12)	0.265 2(9)	0.194 9(6)
C(36)	0.288 3(10)	0.341 3(9)	0.236 9(6)
C(40)	0.631 7(8)	0.405 5(7)	0.343 9(5)
C(41)	0.652 9(9)	0.324 8(7)	0.373 1(5)
C(42)	0.659 1(10)	0.238 0(8)	0.400 5(6)
C(43)	0.678 7(13)	0.160 6(9)	0.369 1(7)
C(44)	0.693 3(15)	0.172 3(9)	0.308 8(7)
C(45)	0.691 4(13)	0.257 7(9)	0.283 0(7)
C(46)	0.669 9(11)	0.331 9(8)	0.315 0(7)

* Atoms whose positional and anisotropic thermal parameters were held invariant for the final two cycles of refinement, owing to the uncertainty of their positions *etc.*, brought about by partial reduction to a hydroxylamino-residue (see text).

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[12] 'International Tables for X-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

Final fractional atomic co-ordinates are listed in Table 1, intramolecular bond distances and bond angles in Table 2, and data relating to least-squares planes of atoms within the molecule in Table 3. Final observed and calculated structure factors and thermal parameters are deposited in Sup-

TABLE 2

Intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Distances

Sn(1)–O(5)	2.067(7)	O(6)–C(20)	1.26(2)
Sn(1)–O(2)	2.062(7)	O(7)–C(20)	1.23(2)
Sn(1)–O(3)	2.063(8)	C(20)–C(21)	1.47(2)
Sn(1)–O(6)	2.056(8)	C(21)–C(22)	1.35(2)
Sn(1)–O(20)	2.047(6)	C(22)–C(23)	1.45(2)
Sn(1)–O(20)	2.058(7)	C(23)–C(24)	1.39(4)
Sn(1)–Sn(1′)	3.148(4)	C(24)–C(25)	1.39(3)
Sn(2)–O(20)	2.113(7)	C(25)–C(26)	1.42(3)
Sn(2)–O(16)	2.430(10)	C(26)–C(21)	1.42(3)
Sn(2)–O(7)	2.436(9)	C(26)–N(3)	1.44(3)
Sn(2)–O(8)	2.409(8)	N(3)–O(11)	1.26(3)
Sn(2)–O(1)	2.661(9)	N(3)–O(13)	1.16(3)
Sn(2)–O(4)	2.596(9)	O(1)–C(30)	1.21(1)
O(20)–O(20′)	2.634(9)	O(5)–C(30)	1.29(1)
O(16)–C(1)	1.45(2)	C(30)–C(31)	1.49(2)
O(16)–C(4)	1.42(3)	C(31)–C(32)	1.37(2)
C(1)–C(2)	1.43(3)	C(32)–C(33)	1.41(2)
C(2)–C(3)	1.54(4)	C(33)–C(34)	1.39(2)
C(3)–C(4)	1.34(3)	C(34)–C(35)	1.40(2)
O(3)–C(10)	1.28(2)	C(35)–C(36)	1.42(2)
O(8)–C(10)	1.21(1)	C(36)–C(31)	1.35(2)
C(10)–C(11)	1.48(2)	C(36)–N(2)	1.50(2)
C(11)–C(12)	1.34(2)	N(2)–O(9)	1.19(2)
C(12)–C(13)	1.45(3)	N(2)–O(10)	1.23(3)
C(13)–C(14)	1.29(2)	O(2)–C(40)	1.30(1)
C(14)–C(15)	1.31(3)	O(4)–C(40)	1.22(1)
C(15)–C(16)	1.41(3)	C(40)–C(41)	1.48(2)
C(16)–C(11)	1.31(2)	C(41)–C(42)	1.40(2)
C(16)–N(4)	1.52(5) *	C(42)–C(43)	1.40(2)
N(4)–O(27)	1.12(4) *	C(43)–C(44)	1.42(3)
N(4)–O(15)	0.99(3) *	C(44)–C(45)	1.37(2)
C(45)–C(46)	1.38(2)	C(46)–C(41)	1.39(2)
C(46)–N(1)	1.44(2)	N(1)–O(12)	1.20(4)
N(1)–O(18)	1.17(4)		

(*b*) Angles

O(2)–Sn(1)–O(6)	84.7(3)	O(1)–Sn(2)–O(4)	76.0(3)
O(2)–Sn(1)–O(3)	89.0(3)	O(1)–Sn(2)–O(8)	145.1(3)
O(2)–Sn(1)–O(5)	172.8(3)	O(4)–Sn(2)–O(8)	70.8(3)
O(2)–Sn(1)–O(20′)	94.5(3)	Sn(2)–O(20)–Sn(1)	126.2(3)
O(2)–Sn(1)–O(20)	90.6(3)	Sn(2)–O(20)–Sn(1′)	127.1(4)
O(6)–Sn(1)–O(3)	79.3(3)	Sn(2)–O(16)–C(1)	125.3(9)
O(6)–Sn(1)–O(5)	89.8(3)	Sn(2)–O(16)–C(4)	124.7(13)
O(6)–Sn(1)–O(20′)	178.9(4)	Sn(2)–O(8)–C(10)	134.5(8)
O(6)–Sn(1)–O(20)	100.9(3)	Sn(2)–O(4)–C(40)	136.5(9)
O(3)–Sn(1)–O(5)	85.5(3)	Sn(2)–O(1)–O(30)	132.6(6)
O(3)–Sn(1)–O(20′)	100.0(3)	Sn(2)–O(7)–C(20)	133.9(8)
O(3)–Sn(1)–O(20)	179.6(3)	C(1)–C(16)–C(4)	108.0(14)
O(5)–Sn(1)–O(20′)	100.0(3)	C(2)–C(1)–O(16)	107.8(18)
O(5)–Sn(1)–O(20)	94.8(3)	C(3)–C(2)–C(1)	105.3(19)
O(20′)–Sn(1)–O(20)	79.9(3)	C(4)–C(3)–C(2)	106.9(21)
Sn(1)–O(20)–Sn(1′)	100.2(3)	O(16)–C(4)–C(3)	111.7(25)
Sn(1)–O(5)–C(30)	123.8(7)	O(3)–C(10)–O(8)	125.7(11)
Sn(1)–O(3)–C(10)	132.2(6)	O(3)–C(10)–C(11)	114.0(9)
Sn(1)–O(6)–C(20)	130.9(7)	O(8)–C(10)–C(11)	120.4(11)
Sn(1)–O(2)–C(40)	124.0(6)	C(10)–C(11)–O(12)	117.8(10)
O(16)–Sn(2)–O(20)	89.5(3)	C(10)–C(11)–C(16)	126.8(14)
O(16)–Sn(2)–O(7)	68.9(3)	C(11)–C(12)–C(13)	120.0(13)
O(16)–Sn(2)–O(1)	140.6(3)	C(12)–C(13)–C(14)	120.9(18)
O(16)–Sn(2)–O(4)	138.8(3)	C(13)–C(14)–C(15)	120.5(18)
O(16)–Sn(2)–O(8)	68.9(3)	C(14)–C(15)–C(16)	117.9(20)
O(20)–Sn(2)–O(7)	82.5(3)	C(15)–C(16)–C(11)	125.1(21)
O(20)–Sn(2)–O(1)	79.4(2)	C(15)–C(16)–N(4)	124.0(21)
O(20)–Sn(2)–O(4)	78.4(3)	C(11)–C(16)–N(4)	110.7(20)
O(20)–Sn(2)–O(8)	83.7(3)	O(15)–N(4)–C(16)	135.9(35)
O(7)–Sn(2)–O(1)	72.1(3)	O(15)–N(4)–O(27)	131.1(61) *
O(7)–Sn(2)–O(4)	145.2(3)	O(27)–N(4)–C(16)	90.8(22) *
O(7)–Sn(2)–O(8)	135.5(3)	C(16)–C(11)–C(12)	145.5(14)
O(6)–C(20)–C(7)	126.2(9)	O(6)–C(20)–C(21)	115.2(11)
O(7)–C(20)–C(21)	118.6(21)	C(20)–C(21)–C(22)	118.1(14)
C(20)–C(21)–C(26)	121.2(12)	C(21)–C(22)–C(23)	122.0(20)
C(22)–C(23)–C(24)	115.9(18)	C(23)–C(24)–C(25)	124.1(20)
C(24)–C(25)–C(26)	117.6(24)	C(25)–C(26)–C(21)	119.8(16)
C(25)–C(26)–N(3)	119.1(18)	C(21)–C(26)–N(3)	120.5(13)
C(26)–N(3)–O(11)	114.7(24)	C(26)–N(3)–O(13)	121.1(19)
O(11)–N(3)–O(13)	123.7(21)	C(26)–C(21)–O(22)	120.6(13)
O(1)–C(30)–O(5)	125.3(10)	O(1)–C(30)–C(31)	121.7(10)
O(5)–C(30)–C(31)	112.9(10)	C(30)–C(31)–C(32)	120.5(9)
C(30)–C(31)–C(36)	122.9(10)	C(31)–C(32)–C(33)	122.5(12)
C(32)–C(33)–C(34)	118.3(13)	C(33)–C(34)–C(35)	121.9(14)
C(34)–C(35)–C(36)	114.9(11)	C(31)–C(36)–C(35)	125.8(11)
C(36)–C(31)–C(32)	116.5(11)	C(35)–C(36)–N(2)	113.8(10)
C(31)–C(36)–N(2)	120.3(11)	C(36)–N(2)–O(9)	117.9(14)
C(36)–N(2)–O(10)	115.8(16)	O(9)–N(2)–O(10)	125.3(15)
O(2)–C(40)–O(4)	123.6(10)	O(2)–C(40)–C(41)	116.0(9)
O(4)–C(40)–C(41)	120.3(10)	C(40)–C(41)–C(42)	120.2(11)
C(40)–C(41)–C(46)	122.2(9)	C(41)–C(42)–C(43)	121.1113
C(42)–C(43)–C(44)	118.5(13)	C(43)–C(44)–C(45)	120.6(15)
C(44)–C(45)–C(46)	118.8(15)	C(45)–C(46)–C(41)	123.3(11)
C(45)–C(46)–N(1)	114.9(16)	C(46)–N(1)–O(12)	116.2(21)
C(46)–N(1)–O(18)	120.4(27)	O(12)–N(1)–O(18)	12.33(23)
C(41)–C(46)–N(1)	121.7(15)		

* Bond lengths and angles calculated for hydroxylamino-group and atomic positions held invariant accordingly (see Table 1). Primes denote symmetry-related atoms.

TABLE 3

Equations of least-squares planes *

In the form: $PI + QJ + RK = S$, where I, J, K are orthogonal co-ordinates in Å related to the monoclinic co-ordinates by: $I = X + Z\cos\beta$, $J = Y$, and $K = Z\sin\beta$. Deviations (Å) of atoms from the planes are listed in square brackets

Plane (1): C(11)—(16)

$$0.076\,96I + 0.843\,45J + 0.531\,67K = -0.861\,34$$

[C(10) 0.041, O(3) 1.201, O(8) 3.726, N(4) −0.030, O(15) −0.21, O(27) −0.054]

Plane (2): C(21)—(26)

$$-0.689\,24I + 0.153\,26J + 0.708\,14K = -4\,024\,24$$

[C(20) 0.075, O(6) −0.795, O(7) 0.970, N(3) −0.174, O(13) −0.857, O(11) 0.578]

Plane (3): C(31)—(36)

$$0.986\,44I - 0.162\,33J - 0.024\,05K = 7.572\,33$$

[C(30) −0.122, O(5) 0.364, O(1) −0.667, N(2) 0.135, O(9) 1.036, O(10) −0.716]

Plane (4): C(41)—(46)

$$0.856\,71I - 0.112\,09J + 0.503\,47K = 4.700\,55$$

[C(40) 2.094, O(3) 2.209, O(4) 0.041, N(1) −0.037, O(18) 0.952, O(12) −1.129]

Plane (5): O(20), O(20′), O(6), O(3)

$$-0.217\,56I - 0.680\,14J + 0.700\,05K = -1.463\,22$$

[O(20) 0.006, O(20′) −0.000, O(6) −0.003, O(3) −0. 003, Sn(1) −0.013]

Plane (6): O(20), O(20′), Sn(1), Sn(1′)

$$-0.190\,46I - 0.679\,89J + 0.708\,15K = -1.252\,98$$

[O(20) −0.027, O(20′) −0.024, Sn(1) 0.029, Sn(1′) 0.022, Sn(2) 0.747, Sn(2′) −0.798]

Plane (7): O(16), O(1), O(4), O(7), O(8)

$$-0.191\,20I - 0.806\,52J + 0.559\,44K = -2.499\,96$$

[O(16) −1.011, O(1) −0.103, O(4) 0.185, O(7) 0.332, O(8) 0.597, Sn(2) 1.373]

* According to V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

plementary Publication No. SUP 21709 (22 pp., 1 microfiche).*

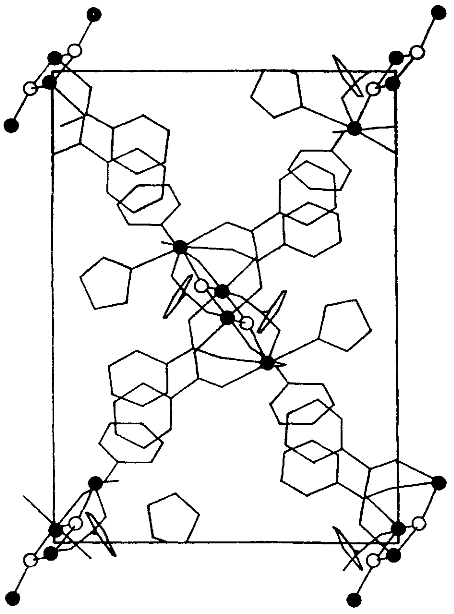

FIGURE 1 View along the *a* axis showing the contents of the unit cell; nitro-groups are omitted for clarity

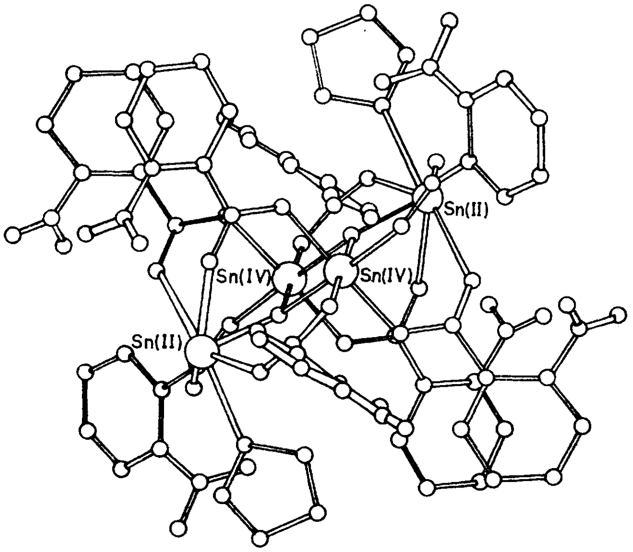

FIGURE 2 Diagram showing the tetranuclear cluster nature of the compound

Variable-temperature Mössbauer Data.—Mössbauer spectra were recorded at temperatures between 77 and 295 K by use of a Harwell spectrometer equipped with a 256 channel analyser and a $Ba^{119m}SnO_3$ source. The temperature control was better than ±1°. Spectra were accumulated until a high-quality spectrum was obtained (minimum counts per channel $>5 \times 10^5$). Data reduction to Lorentzian lineshapes was effected by the usual least-squares methods, and relevant data, including % resonance effects (expressed as relative peak areas), are collected in Table 6 (see later).

DISCUSSION

Crystals of the title compound consist of independent tetranuclear cluster molecules of composition $[Sn^{II}Sn^{IV}(O_2\cdot C_6H_4\cdot NO_2\text{-}o)_4O\cdot(thf)]_2$ (Figure 1). The whole of the molecule is centrosymmetric (Figure 2); Figure 3(a) shows the atom numbering system of the major skeleton and Figure 3(b) (schematically) that of the four crystallographically independent aryl groups.

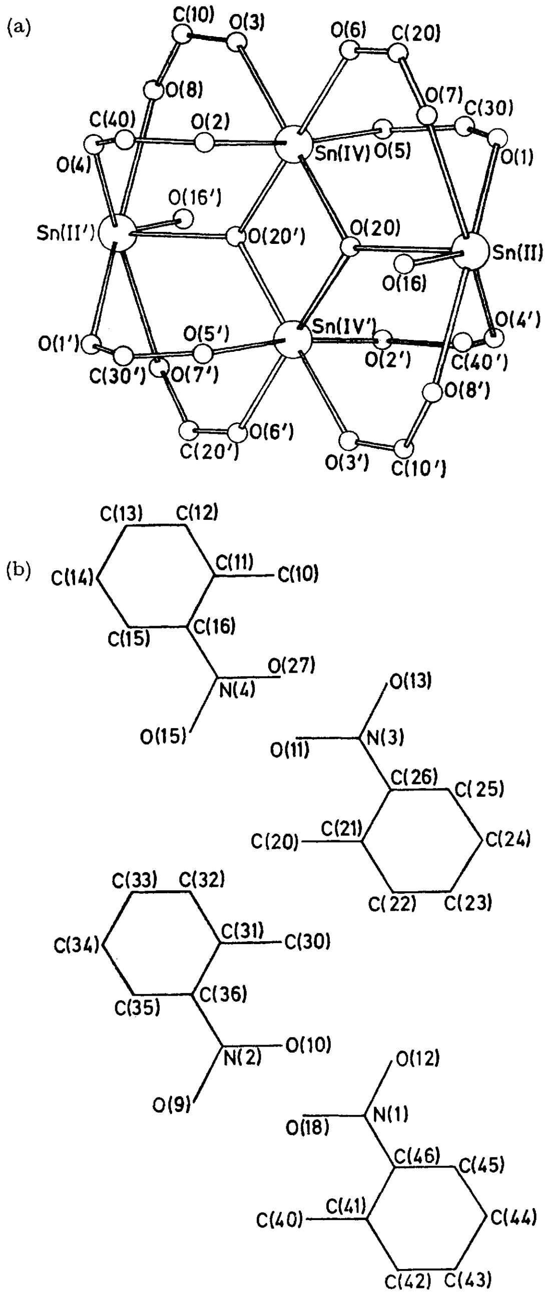

FIGURE 3 Atom numbering of (a) the tetranuclear skeleton, and (b) of the *o*-nitrobenzoato-residues

The two symmetry-related quadrivalent tin atoms are bridged by two oxygen atoms to form a central planar four-membered Sn_2O_2 ring [O–Sn–O 79.9(2), Sn–O–Sn

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

100.2(3)°]. Such ring systems are quite common structural feature of organotin(IV) chemistry, and have been characterised in $[(Me_2SnNCS)_2O]_2$,[13] $[Me_3SiO{\cdot}SnMe_2{\cdot}O{\cdot}SnMe_2{\cdot}O{\cdot}SiMe_3]_2$,[14] $[Me_2Sn(NO_3)(OH)]$,[15] and $[SnCl_3OH(H_2O)]_2{\cdot}3C_4H_8O_2$.[16] The tin–oxygen bond distances within the ring are nearly equal and quite short [*cf.* 2.2 and 2.8 in ref. 14, 1.99(3) and 2.15(4) in ref. 13, 2.06(3) and 2.18(3) in ref. 15, and 2.05(3) and 2.10(3) Å in ref. 16]. Distorted octahedral co-ordination [O–Sn–O bond angles range from 79.3(3) to 100.9(3)°] is completed by four oxygen atoms of four separate *o*-nitrobenzoate groups at slightly longer bond distances [2.056(8)—2.067(7) Å]. All the tin(IV)–oxygen bond distances fall at the short end of the range of such distances measured for other octahedral and carboxylato-tin(IV) derivatives (Table 4).

TABLE 4

Comparison of tin–oxygen bond distances in tin(IV) carboxylate derivatives and other octahedral species

Compound	Co-ordination no.	Geometry	$r(Sn^{IV}–O)$/Å
$Sn_2Ph_4(OAc)_2$ [a]	5	Trigonal bipyramidal	2.25(2), 2.25(2)
$Sn^{IV}(edta)(H_2O)$ [b]	7	Complex ψ-octahedral	2.093(3), 2.088(3), 2.073(4), 2.075(3); $Sn–OH_2$ 2.210(1)
$SnMe_2(C_9H_6NO)_2$ [c]	6	Octahedral	2.11(1), 2.10(1)
$SnMe_2Cl_2{\cdot}2dmso$ [d]	6	Octahedral	2.36(3), 2.35(4)
$SnMe_2Cl_2(C_5H_5NO)_2$ [e]	6	Octahedral	2.25(2)
$Sn(PhCH_2)_3(OAc)$ [f]	5	Distorted trigonal bipyramidal	2.14(2), 2.65(2)
$Sn(C_6H_{10})_3(OAc)$ [g]	4	Distorted tetrahedral	2.12(3), [2.95(4)]
$SnMe_3(OAc)$ [h]	5	Distorted trigonal bipyramidal	2.205(3), 2.391(4)
$SnMe_3(O_2C{\cdot}CF_3)$ [h]	5	Distorted trigonal bipyramidal	2.177(14), 2.458(15)

[a] G. Bandoli, D. A. Clemente, and C. Panattoni, *Chem. Comm.*, 1971, 311. [b] F. P. van Remoortere, J. J. Flynn, and F. P. Boer, *Inorg. Chem.*, 1971, **10**, 2313. [c] E. O. Schlemper, *Inorg. Chem.*, 1967, **6**, 2012. [d] N. W. Isaacs, C. H. L. Kennard, and W. Kitching, *Chem. Comm.*, 1968, 820. [e] E. A. Blom, B. R. Penfold, and W. T. Robinson, *J. Chem. Soc.* (*A*), 1969, 913. [f] N. W. Alcock and R. E. Timms, *J. Chem. Soc.* (*A*), 1968, 1873. [g] N. W. Alcock and R. E. Timms, *J. Chem. Soc.* (*A*), 1968, 1876. [h] H. Chih and B. R. Penfold, *J. Mol. Cryst. Struct.*, 1974, **3**, 285.

TABLE 5

Comparison of tin–oxygen bond distances (Å) in various tin(II) derivatives

Compound	Co-ordination no.	Geometry	$r(Sn–O)$/Å
SnO [a]	4	Square pyramidal	2.21(1)
$SnWO_4$ [b]	6	Distorted octahedral	3 at 2.21(1), 3 at 2.81(1)
$SnCl_2{\cdot}2H_2O$ [c]	3	Trigonal pyramidal	2.325(5)
$SnSO_4$ [d]	3	Trigonal pyramidal	2.51(1), 2 at 2.273(8)
$SnSO_4[SC(NH_2)_2]_2$ [e]	4	Distorted square pyramidal	2.41(2), 2.24(2)
$KSn(O_2CH)_3$ [f]	3	Trigonal pyramidal	2.139(11)—2.182(10)
$Sn[O{\cdot}CPh{\cdot}CH{\cdot}COMe]_2$ [g]	4	Distorted ψ-trigonal bipyramidal	2 at 2.135(1), 2 at 2.290(6)
$Ph_3Sn^{IV}{\cdot}Sn^{II}NO_3$ [h]	5	Distorted square pyramidal	2.38, 2.53, 2.54, 2.84
$Sn(edtaH_2)$ [i]	6	Distorted trigonal prism	2.196(5), 2.343(5), 2.635(5), 3.057(5)
$[Sn_2(edta)]{\cdot}2H_2O$ [j]			
Sn^{I}	6	Distorted ψ-pentagonal bipyramidal	2.14(1), 2.18(1), 2.30(1), 3.10(1), 3.14(1), 3.18(1)
Sn^{II}	7	2 Distorted interlocking tetrahedra	2.29(1), 2.45(1), 2.64(1), 2.70(1)
$[Sn_2(O_2C{\cdot}C_6H_4{\cdot}NO_2)_4O{\cdot}(thf)]_2$ [k]	6	ψ-Pentagonal bipyramidal	2.113(7), 2.43(1), 2.436(9), 2.409(8), 2.661(9), 2.596(9)
$SnHPO_4$ [l]	8		3 at 2.26, 2 at 2.66, 3 at 3.27

[a] W. J. Moore and L. Pauling, *J. Amer. Chem. Soc.*, 1941, **63**, 1392. [b] W. Jeitschko and A. W. Sleight, *Acta Cryst.*, 1972, **B28**, 3174. [c] H. Kiriyama, K. Kitahama, O. Kakamura, and R. Kiriyama, *Bull. Chem. Soc. Japan*, 1973, **46**, 1389. [d] J. D. Donaldson and D. C. Puxley, *Acta Cryst.*, 1972, **B28**, 864. [e] J. D. Donaldson, D. G. Nicholson, D. C. Puxley, and R. A. Howie, *J.C.S. Dalton*, 1973, 1810. [f] A. Jelen and O. Lindquist, *Acta Chem. Scand.*, 1969, **23**, 3071. [g] P. F. R. Ewings, P. G. Harrison, and T. J. King, *J.C.S. Dalton*, 1975, 1455. [h] M. Nardelli, C. Pellizzi, and G. Pellizzi, *J. Organometallic Chem.*, 1975, **85**, C43. [i] K. G. Shields, R. C. Seccombe, and C. H. L. Kennard, *J.C.S. Dalton*, 1973, 741. [j] F. P. van Remoortere, J. J. Flynn, F. P. Boer, and P. P. North, *Inorg. Chem.*, 1971, **10**, 1511. [k] Present work. [l] A. F. Berndt and R. Lamberg, *Acta Cryst.*, 1971, **B27**, 1092.

The geometry at the two crystallographically-equivalent bivalent tin atoms is extremely unusual. It was noted in the preparation that the formation of the compound only took place in thf, and that the use of other solvents resulted in the formation of inhomogeneous products. During crystallisation, a molecule of thf is incorporated into the co-ordination sphere of the bivalent tin to complete (slightly distorted) pentagonal pyramidal co-ordination. The five equatorial positions of the pyramid are occupied by oxygen atoms from the thf molecule and the four carboxylate groups at distances ranging from 2.409(8) to 2.661(9) Å. The equatorial valence O–Sn–O bond angles fall in the range 68.9(3)—76.1(3)°, on both sides of the ideal value of 72°. The apical position of the pyramid is occupied by the bridging oxygen of the four-membered $Sn^{IV}{}_2O_2$ ring, and is thus three-co-ordinated by two quadri- and one bi-valent tin atoms. The tin(II)–apical-oxygen bond distance [2.113(7) Å] is the shortest such distance yet measured. A comparison of the tin(II)–oxygen bond distances in the present compound with those in other bivalent tin–oxygen species is presented in Table 5. Such stereo-

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[13] Y. M. Chow, *Inorg. Chem.*, 1970, **9**, 794.

[14] R. Okawara, *Proc. Chem. Soc.*, 1961, 383.

[15] A. M. Domingos and G. M. Sheldrick, *J.C.S. Dalton*, 1974, 475.

[16] N. G. Bokii and Yu. T. Struchkov, *J. Struct. Chem.*, 1971, **12**, 253.

chemistry has not been observed previously for bivalent tin, and the only other examples of this geometry appear to be in the tris(*O*-ethyl dithiocarbonato)lead(II) [17] and the tris(oxalatoantimoniate) anions.[18] In the tin and antimony species, the metal atom lies substantially below the mean plane of the five equatorial oxygen atoms (Sn 0.32, Sb 0.35 Å) and the O(apical)–Sn–O(eq) bond angles are all reduced from 90° [78.4(3)—89.5(3)°]. Such behaviour is strongly indicative of lone-pair–bond-pair repulsion due to the location of a stereochemically active lone-pair occupying the second apical position of a pentagonal bipyramid. Some corroboration for this hypothesis is available from the molecular packing in the crystal (Figure 1), in which a ' hole ' is apparent to the rear of the tin(II) atom. High co-ordination numbers incorporating stereochemically active lone pairs are, however, not unknown for bivalent tin. In dihydrogen ethylenediaminetetra-acetatostannate(II),[19] the tin(II) atom is located in the middle of a rectangular face of the distorted trigonal prism of four oxygen and two nitrogen atoms, a geometry which is largely determined by the stereochemical demands of the chelating edta ligand. Ditin(II) ethylenediaminetetra-acetate dihydrate,[20] on the other hand, exhibits pseudopentagonal bipyramidal co-ordination at the metal, although in this case the lone pair of electrons is located in an equatorial rather than an axial position, as in the present case. The fundamental question of why the lone pair prefers an equatorial site in some cases but an axial site in others is at present unanswerable. However, the steric demands of the particular ligands may play an important part.

TABLE 6

Temperature–dependent Mössbauer parameters of $[Sn_2(O_2C{\cdot}C_6H_4{\cdot}NO_2\text{-}o)_4O{\cdot}(thf)]_2$

	Sn^{IV}			Sn^{II}						
Temp./K	I.S./mm s^{-1}	Γ/mm s^{-1}	Area	I.S./mm s^{-1}	Q.S./mm s^{-1}	Γ/mm s^{-1}	Area	Γ/mm s^{-1}	Area	Total area
77	0.068	1.183	22.29	3.597	1.823	0.829	7.09	0.869	8.36	15.46
102	0.069	1.127	18.46	3.593	1.824	0.787	5.40	0.869	6.70	12.11
127	0.056	1.104	12.02	3.617	1.839	0.799	3.14	0.833	3.80	6.94
149	0.049	1.057	9.50	3.611	1.844	0.791	2.32	0.846	2.88	5.21
167	0.052	1.074	7.07	3.618	1.845	0.793	1.50	0.950	2.09	3.59
198	0.027	0.997	4.57	3.633	1.810	1.102	1.13	0.73	0.95	2.08
295	−0.021	1.050	2.32	3.906	2.133	1.001	0.39	1.057	0.67	1.07

The four independent carboxylate groups which bridge quadri- and bi-valent tin atoms are of two distinct kinds: two form bridges approximately coplanar with the Sn_2O_2 ring, and two form bridges perpendicular to the ring (Figure 2). However, the bonding parameters of all four residues are essentially the same. In all, the C–O-(Sn^{II}) bond distance [1.21(1)—1.23(1) Å] is slightly shorter than the corresponding C–O(Sn^{IV}) bond distance [1.26(2)—1.30(1) Å], indicating a marginally higher degree of covalent bonding in the Sn^{IV}–O bonds. Bridging carboxylate groups are also observed in $[(OAc)Sn_2Ph_4]$ where the acetate groups bridge the two tin atoms.[21]

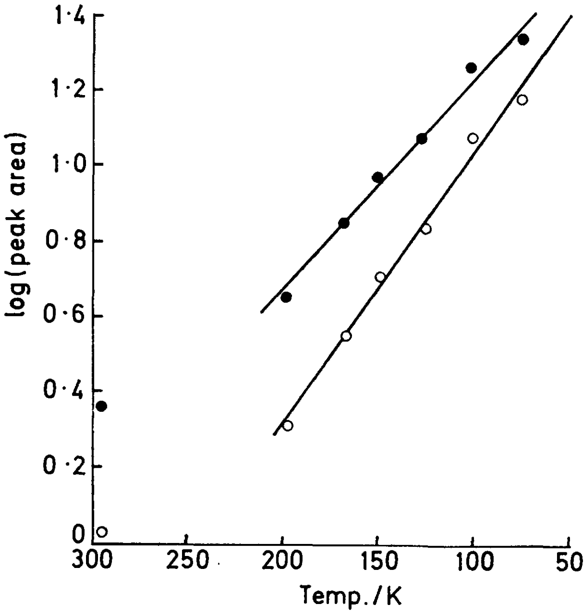

FIGURE 4 Plot of $\log_{10}$ (peak area) *vs.* *T*/K illustrating the differing temperature dependence of the two tin nuclei (full circles Sn^{IV}, open circles Sn^{II})

It was at first thought that the partial oxidation in the compound occurred through the presence of adventitious atmospheric oxidation, but repetition of the experimental procedure under scrupulously anaerobic conditions gave the same result consistently. We now consider that oxidation is due to the presence of the nitro-groups, some of which are partially reduced to hydroxylamino-residues. Reduction of organic nitro-compounds by tin(II) chloride in hydrochloric acid is well known, and the position of the nitro-group in the system *ortho* to the carboxylato-group would place it in a very favourable position close to the tin atom. As noted in the experimental section, some degree of difficulty was encountered in the refinement of one of the nitro-groups [O(27)–N(4)–O(15)], whereas the other three refined to chemically-acceptable positions. As may be seen from Figure 2, the nitro-groups of the two aryl-carboxylate-groups bridging in positions parallel to the Sn_2O_2 ring are in positions

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[17] W. G. Mumme and G. Winter, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 505.

[18] M. C. Poore and D. R. Russell, *Chem. Comm.*, 1971, 18.

[19] K. G. Shields, R. C. Seccombe, and C. H. L. Kennard, *J.C.S. Dalton*, 1973, 741.

[20] F. P. van Remoortere, J. J. Flynn, F. P. Boer, and P. P. North, *Inorg. Chem.*, 1971, **10**, 1511.

[21] G. Bandoli, D. A. Clemente, and C. Panattoni, *Chem. Comm.*, 1971, 311.

more favourable for oxidation than are the two carboxylato-groups in perpendicular bridging positions; it is in the nitro-group of one of the former type that refinement was poor, and gave chemically-unacceptable, low values for the N–O bond distances. Attempted refinement treating this as a pure hydroxylamino-group was equally unsuccessful, indicating a situation intermediate between the two extremes. Such behaviour would be expected for partial reduction of this nitro-group to a hydroxylamino-residue.

Temperature-dependent Mössbauer Effect.—The different nature of the binding of the bi- and quadri-valent tin atoms is reflected in the temperature dependence of the recoil-free fraction of the resonances due to the two tin atoms in the tin-119m Mössbauer spectrum. The recoil-free fractions of the two tin atoms are unequal (Table 6), implying a significantly different lattice vibrational spectrum for each.

The temperature dependence of the resonance effect of the two different valence-state tin atoms is shown in Table 6. Assuming a Debye model for the phonon spectrum, when $T > (\theta_{\Delta}/2)$, one obtains the expression: $f \simeq \exp(-6E_r/k^2)T$, where f is the recoil-free fraction, E_r the recoil energy of the free nucleus, θ_D the Debye temperature, and k the Boltzmann constant.

The recoil-free fraction f is directly proportional to the percentage area under the curve of each resonance. Therefore a plot of log(area) *vs.* T gives a straight line of gradient $[-6E_r/k^2]\cdot\log_e 10$ (Figure 4). Taking the value 0.258×10^{-2} eV for the recoil energy of ^{119}Sn, values of 119.6 and 104.1 K may be estimated for the Debye temperatures of the Sn^{IV} and Sn^{II} atoms, respectively. These results are in accordance with the crystallographic data, *i.e.* tin(IV) atoms are more strongly held in the lattice than are tin(II) atoms, and consequently have a higher Debye temperature, the temperature at which lattice vibrations cease.

[5/1919 *Received, 2nd October*, 1975]