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The Synthesis and Crystal Structure of Potassium-μ-Oxalato-Di[trisoxalatostannate(IV)] Tetrahydrate

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A simplified procedure for the synthesis of $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ is reported. The crystal structure of this complex has been determined by X-ray diffraction. There are two molecules in the monoclinic unit cell, space group $P2_1/n$, with $a = 13.88(1)$, $b = 12.84(1)$, $c = 8.94(1)$ Å, $\beta = 98.01(8)°$. Full-matrix least-squares refinement with 1931 diffractometer-collected reflections reduced R to 0.030. The tin is seven-coordinated and the coordination geometry is best described as tetragonal base–trigonal base. The average Sn–O distance is 2.116 Å. The bridging oxalate ion coordinates with the two tin atoms in a 1,2-trans-conformation. The water molecules are present as free molecules and are not bonded to the metal atoms.

Introduction

A recent investigation of the photolysis of trisoxalatogermanate(IV) in aqueous solution[1,2] has created interest in the photochemical process for oxalato complexes of tin(IV). Since limited information concerning the synthesis and structure of such complexes is available, the present investigation was undertaken.

Dey and Bhattacharya[3–5] reported conductometric and spectroscopic evidence for the existence of the complex species $Sn(C_2O_4)_2$ and $H_4Sn(C_2O_4)_4$ or $Sn(C_2O_4)_4^{4-}$ in aqueous mixtures of $SnCl_4$ and $H_2C_2O_4$ or $K_2C_2O_4$ respectively. Willard and Toribara[6] succeeded in isolating a complex with formula $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ using a time-consuming procedure with metallic tin as starting material. Dean *et al.*[7] prepared a trisoxalato complex having the formula $[(CH_3CH_2)_4N]_2Sn(C_2O_4)_3$.

TABLE I. Chemical Analysis of $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$.

Analysis	Analytical Technique	Theoretical %	Experimental %
K	Flame Photometry (Lange)	20.22	20.24
Sn	Atomic Absorption Spectrophotometry (Varian Techtron AA6)	20.46	20.47
C	C H N Analyses	14.49	14.49
H	(Hewlett Packard Model 185B)	0.70	0.69
C_2O_4	$KMnO_4$ Titration[9]	53.11	53.09

We have found an extremely simple method for the synthesis of $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$, the formula being assigned after thorough chemical analyses of the crystalline product and the determination of the crystal structure by X-ray diffraction.

Experimental

Synthesis and Analysis of $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$

2 cm^3 (0.017 mol) of fuming $SnCl_4$ is slowly added to a magnetically stirred solution of 10.94 g (0.059 mol) $K_2C_2O_4 \cdot H_2O$ in 150 cm^3 distilled water. The mixture is then heated to 70° C and 150 cm^3 absolute ethanol at room temperature added to the hot solution. The oxalate solution should not be heated prior to the addition of $SnCl_4$ since the latter is thermally unstable[8]. Upon cooling, large acicular crystals separate. These are filtered on a sintered glass crucible and washed with 50 cm^3 ice-cold absolute ethanol followed by 50 cm^3 ice-cold diethyl ether. The washed product (*ca.* 80% yield) may be recrystallized by dissolving it in 50 cm^3 distilled water at 70° C and adding 50 cm^3 absolute ethanol at room temperature to the hot solution. The final product obtained upon cooling is filtered, washed with 25 cm^3 quantities of ice-cold absolute ethanol and diethyl ether, and dried in an oven at 70° C. A recrystallized sample of the complex was analysed by means of the analytical techniques indicated in Table I. The results are in very good agreement with the theoretical values.

X-ray Intensity Measurements

Lattice parameters were determined and intensities collected with a crystal, cut and ground to roughly spherical shape, with a diameter of 0.2 mm.

Intensity data were collected at room temperature on a Philips PW1100 four-circle diffractometer using graphite-monochromated Mo-K_α radiation. Accurate unit cell and orientation parameters were obtained from a least-squares fit of the Θ, χ and φ values of 25 high-angle reflections. Intensity data were collected in the Θ range 3° to 22° by the ω–2Θ scan technique at a scan rate of 0.04° s^{-1} and a constant scan width of 1.4°. The intensities and peak positions of three standard reflections were remeasured at hourly intervals and showed no significant change during data collection. Of the 1931 independent reflections measured, 217 were considered unobserved with $I < 3\sigma(I)$ where $\sigma(I) = [(0.025)^2 + S + B]^{1/2}$, S = scan count and B = total background count. The background was counted for half the scanning time on each side of a reflection. No absorption corrections were made as the corrections for a spherical crystal are virtually constant over the experimental Θ range.

Structure Analysis and Refinement

The complex is required to have a centre of symmetry as there are two formula-units per unit cell and four equivalent positions for the space group. The structure was determined by the heavy atom method. The position of the tin atom was determined from a three-dimensional Patterson synthesis. The remaining non-hydrogen atoms were located through subsequent Fourier syntheses. The structure was refined by the full-matrix least-squares technique, minimizing the

TABLE II. Crystal Data for $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$.

$K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$	
M.W. = 1160.22	
Crystallographic System:	Monoclinic
Systematic Absences:	h0l: h+l = 2n+1
	0k0: k = 2n+1
Space Group:	$P2_1/n$
Cell Parameters:	a = 13.88(1) Å
	b = 12.84(1) Å
	c = 8.94(1) Å
	β = 98.01(8)°
	V = 1578.4 $Å^3$
F_{000} = 1124	Z = 2
d_c = 2.441 g cm^{-3}	$\mu(\text{Mo } K_\alpha)$ = 25 cm^{-1}
d_x = 2.45(1) g cm^{-3}	λ = 0.7107 Å

TABLE III. Final Fractional Coordinates (× 10^4) and Anisotropic Temperature Factors ($Å^2$ × 10^4)[a] with e.s.d.'s in Brackets.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	7201(1)	4398(1)	3396(1)	159(2)	182(3)	172(2)	2(2)	20(2)	–10(2)
K(1)	9761(1)	2063(1)	7248(2)	217(7)	348(9)	247(8)	14(7)	–1(6)	50(7)
K(2)	7779(1)	2467(1)	0300(2)	403(9)	218(8)	317(9)	–13(7)	103(7)	–25(7)
K(3)	8072(1)	5438(1)	7656(2)	412(9)	426(10)	282(9)	103(7)	–5(7)	–135(7)
C(1)	6260(4)	4935(5)	0313(7)	237(34)	295(39)	188(38)	–48(30)	14(27)	62(32)
C(2)	6249(4)	5953(5)	1235(7)	187(33)	225(38)	275(40)	–43(29)	60(29)	35(31)
C(3)	7038(4)	2220(5)	4400(7)	126(31)	230(40)	255(37)	37(27)	57(26)	–13(30)
C(4)	7527(4)	2830(5)	5803(7)	154(31)	230(38)	255(37)	23(27)	65(27)	–1(31)
C(5)	9029(5)	5583(5)	3937(7)	252(38)	252(37)	276(36)	2(32)	–64(29)	123(31)
C(6)	9168(5)	4744(5)	2744(7)	282(39)	280(39)	297(37)	15(31)	–22(31)	71(31)
C(7)	5555(4)	5037(5)	4940(7)	203(32)	213(36)	178(32)	16(29)	78(26)	21(30)
O(11)	6570(3)	4131(3)	1104(5)	313(25)	252(26)	210(24)	33(20)	–25(20)	–28(21)
O(12)	6009(4)	4929(4)	–1041(5)	680(35)	439(32)	192(28)	–28(27)	–65(23)	38(24)
O(21)	6665(3)	5875(3)	2609(4)	305(24)	222(24)	199(25)	25(19)	5(20)	40(19)
O(22)	5879(3)	6743(4)	660(5)	332(26)	299(28)	373(27)	59(22)	–6(21)	125(23)
O(31)	6933(3)	2764(3)	3169(4)	252(22)	175(22)	136(22)	1(18)	2(17)	11(18)
O(32)	6792(3)	1319(3)	4500(5)	386(27)	197(27)	307(26)	–83(21)	43(20)	27(20)
O(41)	7658(3)	3800(3)	5591(4)	278(23)	231(27)	177(23)	–13(19)	–34(18)	4(19)
O(42)	7769(3)	2365(3)	7002(5)	300(24)	374(27)	190(25)	33(21)	–27(19)	78(22)
O(51)	8207(3)	5524(3)	4469(4)	162(22)	230(24)	273(24)	–41(18)	6(18)	–50(19)
O(52)	9665(3)	6223(4)	4292(5)	299(26)	373(29)	512(31)	–187(24)	–219(23)	4(24)
O(61)	8448(3)	4099(3)	2436(5)	202(23)	281(25)	293(25)	–12(20)	53(18)	–58(20)
O(62)	9922(3)	4712(4)	2169(5)	178(25)	621(35)	474(30)	–9(23)	160(22)	0(26)
O(71)	5822(3)	4337(3)	4041(4)	164(21)	249(24)	264(24)	–5(18)	77(18)	–18(20)
O(72)	6074(3)	5691(3)	5619(5)	231(23)	340(27)	270(25)	–88(22)	63(19)	–99(22)
$H_2O(1)$	5900(5)	2571(6)	8143(8)	680(41)	1063(57)	1130(57)	–201(39)	552(40)	–478(46)
$H_2O(2)$	4452(6)	1535(8)	4543(9)	1151(60)	2477(99)	1620(80)	1331(70)	1067(59)	1585(81)

[a] Thermal parameters are of the form $T = \exp[-2\pi^2(a^{*2}h^2U_{11} + \ldots + 2b^*c^*klU_{23})]$.

quantity $\Sigma\omega(\Delta F)^2$ with $1/\sigma_F{}^2$ weights. Isotropic refinement reduced the unweighted residual to 0.053. With all the atoms refined anisotropically the discrepancy-indices $R = \Sigma\Delta F/\Sigma F_o$ and $R_\omega = [\Sigma\omega(\Delta F)^2/\Sigma\omega F_o{}^2]^{1/2}$ converged to final values of 0.030 and 0.038 respectively. The hydrogen atoms were not resolvable as a difference synthesis calculated after the final cycle of refinement was essentially featureless with a largest peak of 0.80 e Å^{-3}. In the last cycle of refinement the largest parameter-shift was less than 0.1 times its standard deviation.

All calculations were done with the X-RAY system of crystallographic programs[10]. The scattering factors for all the atoms were generated from the analytical expressions of Cromer and Mann[11]. The components of the anomalous dispersion-correction to the scattering factors of tin and potassium are those given by Cromer and Liberman[12].

TABLE IV. Bond Lengths (Å) and Angles (°) with e.s.d.'s in Brackets.

(a) Bond Lengths:

Sn–O(11)	2.142(5)	C(1)–O(11)	1.291(7)
Sn–O(21)	2.121(4)	C(1)–O(12)	1.212(8)
Sn–O(31)	2.136(4)	C(2)–O(21)	1.286(7)
Sn–O(41)	2.121(4)	C(2)–O(22)	1.218(8)
Sn–O(51)	2.142(5)	C(3)–O(31)	1.295(7)
Sn–O(61)	2.073(4)	C(3)–O(32)	1.213(8)
Sn–O(71)	2.075(4)	C(4)–O(41)	1.277(7)
C(1)–C(2)	1.547(9)	C(4)–O(42)	1.232(7)
C(3)–C(4)	1.553(8)	C(5)–O(51)	1.297(8)
C(5)–C(6)	1.547(9)	C(5)–O(52)	1.215(8)
C(7)–C(7)′	1.563(8)	C(6)–O(61)	1.298(8)
		C(6)–O(62)	1.229(8)
		C(7)–O(71)	1.294(7)
		C(7)–O(72)	1.212(7)
Average Sn–O	2.116	Average C=O	1.219
Average C–C	1.553	Average C–O	1.291

(b) Angles around Sn:

	O(21)	O(31)	O(41)	O(51)	O(61)	O(71)
O(11)	75.4(2)	73.1(2)	149.0(2)	133.7(2)	80.0(2)	89.5(2)
O(21)		143.0(2)	132.6(2)	73.9(2)	107.6(2)	80.4(2)
O(31)			76.0(2)	143.1(2)	85.6(2)	80.5(2)
O(41)				74.8(2)	99.0(2)	84.1(2)
O(51)					77.3(2)	118.1(2)
O(61)						164.5(2)

(c) O–O Distances in Coordination Polyhedron:

O(11)–O(21)	2.606(6)	O(31)–O(41)	2.620(6)
O(11)–O(31)	2.547(6)	O(31)–O(61)	2.859(6)
O(11)–O(61)	2.711(6)	O(31)–O(71)	2.721(6)
O(11)–O(71)	2.968(6)	O(41)–O(51)	2.589(6)
O(21)–O(51)	2.561(6)	O(41)–O(61)	3.190(6)
O(21)–O(71)	2.707(6)	O(41)–O(71)	2.812(6)
		O(51)–O(61)	2.634(6)

(d) Bond Angles in the Oxalate Ligands:

Central Atom	O–C–O	C–C–O(1)	C–C–O(2)
C(1)	124.8(6)	114.2(5)	121.0(6)
C(2)	125.1(6)	114.0(5)	120.9(5)
C(3)	125.3(5)	113.6(5)	121.2(5)
C(4)	125.1(5)	115.3(5)	119.6(5)
C(5)	126.0(6)	114.4(5)	119.7(6)
C(6)	124.4(6)	115.1(6)	120.5(6)
C(7)	126.3(5)	111.7(5)	122.0(5)
Average	125.3	114.0	120.7

Discussion

The proposed synthesis is based on mixing $SnCl_4$ and $K_2C_2O_4$ in the ratio 1:3.5. The product is the same when isolated from a 1:4 mixture, supporting the statement of Willard and Toribara[6] that tin(IV) does not form an oxalato complex other than $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ at ratios exceeding 1:3.5. It thus seems that the complex species suggested by Dey and Bhattacharya[3–5], do only exist in aqueous solution or form by dissociation of $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ under such conditions. A paper concerning an investigation into the manner in which this complex exists in aqueous solution, is published separately[13].

The crystal data for $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ are summarized in Table II and the calculated and observed structure factors on a 10 times absolute scale are listed in a table available from the Editor. The refined atomic parameters are listed in Table III, and selected interatomic distances and angles are given in Table IV.

Figure 1 illustrates the configuration of the anion and the numbering of the atoms. The unit cell contents is shown in Figure 2, and Figure 3 contains a schematic diagram of the coordination polyhedron. It is concluded that the complex $K_6Sn_2(C_2O_4)_7 \cdot 4H_2O$ exists in the crystalline state as centrosymmetric oxalato-bridged anions surrounded by potassium cations. The water molecules are not directly bonded to the central tin atoms but are present in the crystal lattice as water of crystallization. The coordination polyhedron around the seven-coordinated tin atom, is formed by one oxygen atom from the bridging oxalate-ion and two each from the three other bidentate oxalate-ligands as shown in Figure 1. The geometry of the polyhedron (Figure 3) is close to that of a monocapped trigonal prism, but because of the absence of C_{2V} symmetry, it can best be described as tetragonal base–trigonal base. The deviations from the least-squares planes given in Table V and the small spread of Sn–O bond lengths indicate that the geometry cannot be described in terms of a pentagonal-bipyramidal structure. The allocation of polyhedron vertices to the tetragonal base–trigonal base model can be done in two ways. Taking the cap to be atoms O(31), O(41) and O(71), the angle between the basal plane and the cap is 6.3°. If the cap is formed by O(31), O(11) and O(61), the interplanar angle is 5.6°.

The potassium ions are each surrounded by nine oxygen atoms (from water and oxalate ions) with contact distances that vary between 2.661 and 3.227 Å

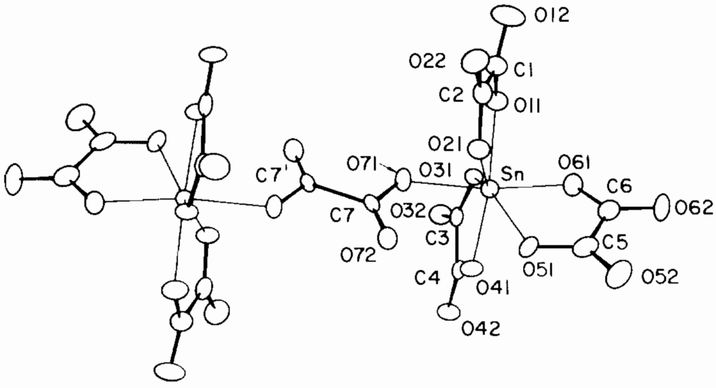

Figure 1. Perspective view[14] of the $[Sn_2(C_2O_4)_7]^{6-}$ anion. Thermal ellipsoids are scaled to 50% probability.

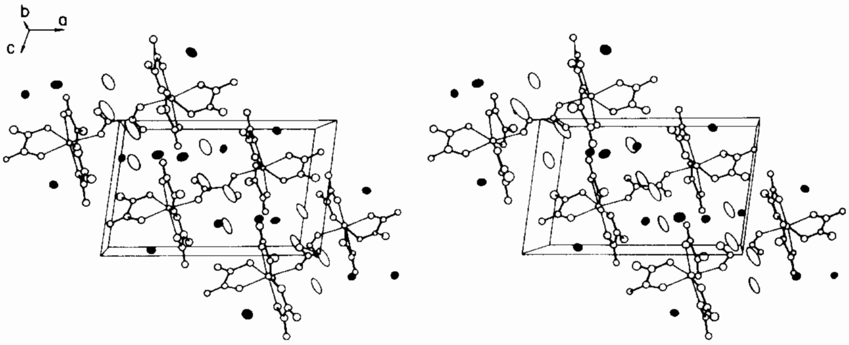

Figure 2. Stereo diagram[14] of the unit cell and surrounding molecules, viewed down the *b*-axis. The *a*-axis is horizontal, the *c*-axis vertical down. Potassium ions are represented by solid ellipsoids and water molecules by open ellipsoids.

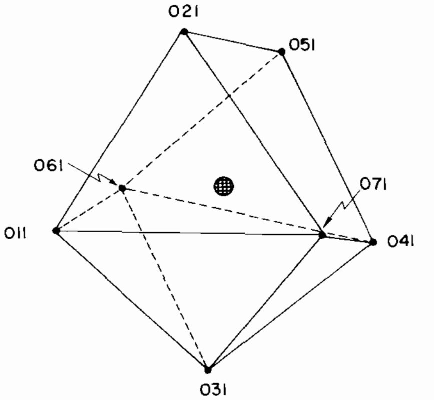

Figure 3. Respective view[14] of the coordination polyhedron around a tin atom.

for K(1), 2.805 and 3.023 Å for K(2), and 2.776 and 3.470 Å for K(3). The coordination polyhedra so formed are of irregular shape. The contacts between water molecules and other atoms are listed in Table VI. The differences in the types of contacts suggest that the structure is stabilized by the water molecules. The range of H_2O–O and K–H_2O distances indicates relatively weak hydrogen bonding. The absence of hydrogen atom positions unfortunately prevents a full description of the hydrogen bonding network. The dimensions of the oxalate groups are insensitive to coordination as the reported bond lengths and angles (Table IV) are very close to those observed for oxalic acid[15]. The angles subtended at the metal by these groups are 75.4, 76.0 and 77.3°.

TABLE V. Least-squares Planes[a,b].

	1	2	3	4	5	6
Atom 1	O(11)	O(11)	O(21)	O(11)	O(31)	O(11)
Atom 2	O(21)	O(21)	O(41)	O(41)	O(41)	O(31)
Atom 3	O(31)	O(51)	O(51)	O(61)	O(71)	O(61)
Atom 4	O(41)	O(61)	O(71)	O(71)		
Atom 5	O(51)					
A	12.632	6.726	–4.907	1.505	7.191	–4.398
B	–1.634	7.468	7.532	12.719	8.221	8.508
C	–4.624	–6.390	6.894	0.614	–5.669	6.405
D	6.815	6.995	3.081	6.478	5.461	1.333
Δ 1	0.299	–0.196	–0.128	–0.168	0.000	0.000
Δ 2	–0.561	0.209	–0.122	–0.150	0.000	0.000
Δ 3	0.026	–0.205	0.134	0.156	0.000	0.000
Δ 4	–0.348	0.192	0.115	0.162		
Δ 5	0.584					

	7[d]	8[d]	9[d]	10[d]
Atom 1	Sn	Sn	Sn	Sn
Atom 2	C(1)	C(3)	C(5)	C(7)
Atom 3	C(2)	C(4)	C(6)	C(7)[c]
Atom 4	O(11)	O(31)	O(51)	O(71)
Atom 5	O(12)	O(32)	O(52)	O(72)
Atom 6	O(21)	O(41)	O(61)	O(71)[c]
Atom 7	O(22)	O(42)	O(62)	O(72)[c]
A	13.154	13.070	–4.411	–1.325
B	2.972	–3.175	7.813	8.073
C	–3.121	–3.192	–6.044	–6.716
D	9.610	7.093	–2.000	0.015
Δ 1	0.109	–0.163	0.207	0.301
Δ 2	–0.007	–0.003	0.000	–0.002
Δ 3	–0.006	–0.006	0.004	0.000
Δ 4	–0.084	0.080	–0.006	0.001
Δ 5	0.085	–0.070	0.004	0.000
Δ 6	0.090	–0.075	0.004	0.000
Δ 7	–0.078	0.075	–0.007	0.000

[a] The planes are defined by the equation Ax + By + Cz = D. [b] Δi refers to the deviation (in Å) of atom i from the least-squares plane. [c] Related through the centre at (1/2, 1/2, 1/2). [d] Plane determined by atoms 2 to 7, unlike the other planes which are determined by all the atoms given.

TABLE VI. Intermolecular Contacts (Å).

(a) Shortest Contacts Involving the Anion only:

Contact	Position[a]	Distance
C(2)–C(3)	3/ 1 0 0	3.001
C(2)–O(32)	3/ 1 0 0	2.924
C(3)–O(22)	3/ 1–1 0	2.964
C(4)–O(22)	3/ 1–1 0	3.060
C(6)–O(32)	3/ 1 0 0	3.025
O(21)–O(32)	3/ 1 0 0	3.098

(b) Shortest Contacts Involving the Water Molecules:

$H_2O(1)$			$H_2O(2)$		
Contact	Position[a]	Distance	Contact	Position[a]	Distance
O(42)	1/ 0 0 0	2.929	O(62)	4/–1 0 0	2.842
O(22)	2/ 1 1 1	2.959	O(62)	3/ 1–1 0	2.992
O(52)	3/ 1–1 1	3.061	O(61)	4/–1 0 0	3.210
O(12)	1/ 0 0 1	3.114	O(32)	1/ 0 0 0	3.265
O(62)	4/–1 0 0	3.296	O(42)	4/–1 0–1	3.338
K(2)	1/ 0 0 1	3.024	K(1)	4/–1 0–1	2.808
K(3)	3/ 1–1 1	3.215	K(2)	4/–1 0 0	2.817
C(4)	1/ 0 0 0	3.303	K(3)	4/–1 0–1	3.470
O(11)	1/ 0 0 1	3.347	C(6)	4/–1 0 0	3.371

[a] In the symmetry code u/x y z; x, y and z refer to cell translations and u refers to the transformations
1. x, y, z
2. –x, –y, –z
3. $^1/_2$–x, $^1/_2$+y, $^1/_2$–z
4. $^1/_2$+x, $^1/_2$–y, $^1/_2$+z.

Structural studies on organotin(IV) compounds show that tin(IV) is capable of forming four-, five-, six-, seven- and eight-coordinate complexes (ref. 16 to 18 and literature cited). The structures of seven-coordinate organotin(IV) complexes are reported as distorted monocapped trigonal–prismatic[16] for stannic ethylenediaminetetraacetate monohydrate, roughly pentagonal-bipyramidal[19] for tris(tropolonato)monochloro and tris(tropolonato)monohydroxotin(IV) and pentagonal-bipyramidal[17] for μ-oxalato-bis[(di-n-propyl sulphoxide)nitratodiphenyltin(IV)]. The reported structure of potassium-μ-oxalato-di[trisoxalatostannate(IV)] tetrahydrate is an example in which the seven-coordinate character of Sn(IV) can best be described as tetragonal base–trigonal base.

The oxalate bridges between coordination polyhedra usually bond as bichelates (*i.e.* tetradentate) to form two five-membered rings with the metal atoms[17, 18, 20]. In this case, however, the oxalate bridge is attached to each metal atom by one bond only, the other oxygen being at a Sn–O distance of 3.165(5) Å. The formation of five-membered rings is prevented by the 1,2-*trans*-configuration of the bridging group. This is also reflected in the reported bond lengths (Table IV). The C(7)–O(71) distance (*i.e.* C–O) of 1.294(7) Å and C(7)–O(72) distance (*i.e.* C = O) of 1.212(7) Å should be approximately equal (*ca.* 1.25 Å) if the oxalate bridge participates as a tetradentate ligand[20].

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