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Synthesis, Properties and Crystal Structure of β-SnWO$_4$

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SnWO$_4$ has been prepared by reaction of SnO and WO$_3$ in evacuated silica capsules. It crystallizes in two modifications which transform into each other by a fast but diffusion-controlled phase transition at 670°C. Rapid quenching from above that temperature yields diamagnetic and semiconducting β-SnWO$_4$ which is cubic ($P2_13$–T^4), $a=7{\cdot}2989$ (3) Å and $Z=4$. The structure has been solved and refined from single-crystal counter data. The R value is 0·034 for 248 observed reflections. The tungsten atom is located in a fairly regular oxygen tetrahedron. Sn^{2+} is coordinated to six oxygen atoms forming three short (2·21 Å) and three long (2·81 Å) bonds with a configuration characteristic of a 'lone pair' cation. The structure of β-SnWO$_4$ is discussed and compared with that of related compounds.

Introduction

Little is known about the crystal chemistry of divalent tin in ternary oxides of transition metals. This may be due to the low stability of this oxidation state, which requires preparation of Sn^{2+} oxides to be carried out in closed systems, or to the tendency of Sn^{2+} to disproportionate, especially at higher temperatures as is known for SnO. However Sn$_2^{2+}$Nb$_2$O$_7$ and Sn$_2^{2+}$Ta$_2$O$_7$ are reported to have the pyrochlore structure and to be stable to at least 750°C (Gasperin, 1955, 1960; Brisse, 1967). Recently tungsten bronzes of the type Sn$_x$WO$_3$ were prepared (Gier, Pease, Sleight & Bither, 1968) and Mössbauer experiments showed that tin is present as Sn^{2+} (McColm, Steadman & Howe; 1970).

We have succeeded in preparing SnWO$_4$ in two modifications. Neither form has been previously reported, and our structure determinations show that both modifications contain divalent tin.

This paper gives details about preparation, properties, and structure of high-temperature β-SnWO$_4$. Work on low-temperature α-SnWO$_4$ is still in progress and will be reported at a later time.

Synthesis and properties

Stannous tungstate was prepared from an equimolar mixture of SnO and WO$_3$ or from a 3SnO$_2$+2WO$_3$+1W mixture. The reagents were of the highest purity commercially available; SnO was reagent grade, and Sn, WO$_3$, and W had listed purities of better than 99·99%. Intimate mixtures of the appropriate quantities of reactants were sealed in evacuated silica ampoules which were heated at 600 to 900°C for one to ten hours.

DTA experiments show that SnWO$_4$ melts at 782°C and has a transition at about 670°C. Thus, α-SnWO$_4$ is obtained if the heat treatment is below 670°C, and β-SnWO$_4$ can be obtained at room temperature by rapidly quenching (*e.g.* in ice water) the sealed silica tubes from above 670°C. The heat required to transform α- to β-SnWO$_4$ is about half that needed to melt β-SnWO$_4$. Small crystals of β-SnWO$_4$ were found in samples which were slow-cooled from 800 to 700°C and then rapidly quenched. Heating β-SnWO$_4$ at 400°C for 1 hr did not lead to a detectable conversion to α-SnWO$_4$. However, after $\frac{1}{2}$ hour at 500°C, β-SnWO$_4$ was completely converted to α-SnWO$_4$.

β-SnWO$_4$ is diamagnetic and semiconducting. Four-probe electrical resistivity measurements on a single crystal gave a room temperature resistivity of 3×10^4 Ohm.cm and an activation energy of 0·1 eV.

Optical reflectance spectra recorded from a powdered sample show significant absorption uniformly throughout the entire visible region with a peak in the near UV region. Thus, large crystals of β-SnWO$_4$ appear black, while small crystals are clear white. The 'black' color may be due to the Sn^0 which could be present in very small amounts associated with crystal imperfections, *e.g.* as Ag^0 in AgCl. Similarly Sn^{4+} might exist at imperfections which could lead to charge transfer between Sn^{2+} and Sn^{4+}. The index of refraction was not determined; however, it was found to be greater than 2·0 (Becke line method).

Structure determination

Unit cell and space group

Small irregularly shaped crystals were examined with a Buerger precession camera using Mo $K\alpha$ radiation. They have cubic symmetry, Laue group $m3$. The only extinction condition – reflections $h00$ are present for $h=2n$ only – leads to space group $P2_13$–T^4. A lattice constant $a=7{\cdot}2989$ (3) Å was obtained by a least-squares refinement of data recorded with a Guinier–Hägg camera (Table 1). High purity KCl ($a=6{\cdot}29310$ Å) was used as internal standard. The calculated density is 7·43 g.cm^{-3} assuming 4 formula units per unit cell.

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* Contribution No. 1913.

Table 1. *Evaluation of a Guinier–Hägg powder pattern of β*-$SnWO_4$

Cu $K\alpha$ radiation, calculated data were generated by a computer program (Yvon, Jeitschko & Parthé, 1969) from the final structure.

hkl	d_c	d_o	I_c	I_o
110	5.1611	5.1588	5	vw
111	4.2140	4.2123	8	w
200	3.6495	3.6494	29	s
210 120	3.2642	3.2660	100	vvs
211	2.9798	2.9810	38	s
220	2.5806	2.5805	3	vw
221	2.4330	2.4330	11	w
310 130	2.3081	2.3083	1	vvw
311	2.2007	2.2007	8	w
222	2.1070	2.1070	1	vvw
320 230	2.0244	2.0245	1	vvw
321 231	1.9507	1.9511	50	vs
400	1.8247	1.8248	6	w
410 140 322	1.7702	1.7704	17	m
411 330	1.7204	1.7206	9	w
331	1.6745	1.6746	14	m
420 240	1.6321	1.6321	4	vw
421 241	1.5928	1.5930	15	m
332	1.5561	1.5566	<1	vvw
422	1.4899	1.4899	1	vvw
430 340	1.4598	1.4599	1	vvw
510 150 431 341	1.4314	1.4315	21	s
511 333	1.4047	1.4048	13	m
520 250 432 342	1.3554	1.3554	12	m
521 251	1.3326	1.3327	10	w
440	1.2903	1.2904	2	vw
441 522	1.2706	1.2707	9	w

Intensity data

The linear absorption coefficient of β-$SnWO_4$ for Mo $K\alpha$ radiation is 375 cm^{-1}. Thus transmission of Mo $K\alpha$ radiation through 1μm of β-$SnWO_4$ results in an intensity loss of about 4%. It is clear that for a rigorous treatment of absorption the dimensions of the crystal need to be known quite accurately. Since crystals defined by flat surfaces were not available, we used a very small crystal, so that the total absorption was low and the shape of the crystal was less important. It was approximately spherical with an average radius of about 8μm. Intensities were measured with an automated Picker single-crystal diffractometer. Graphite monochromated Mo $K\alpha$ radiation was used with scintillation counter and pulse-height discriminator. The scans were along 2θ extending over 1·5° plus the angular separation of the $K\alpha$ doublet. Scan speed was 0·3° 2θ/min. Background was counted for 2 min at beginning and end of the scans. The intensity of a standard reflection measured every 5 hr varied between ±1·8% during the period of data collection. Reflections for two octants up to $(\sin\theta)/\lambda = 0{\cdot}85$ were measured and the six equivalent reflections were averaged. An approximate correction for absorption was made assuming spherical shape of the crystal (*International Tables for X-ray Crystallography*, 1959). Lorentz–polarization correction was done as described earlier (Jeitschko, 1971).

To estimate the seriousness of absorption errors due to deviations from spherical crystal shape, equivalent reflections were compared before averaging. The strongest and weakest reflections within each group of equivalent reflections differed on the average by ±15% in intensity for the 50 strongest unique reflections, with no difference greater than ±22%. Because of poor counting statistics due to the relatively small crystal volume these differences were of course much greater for weak reflections.

Solution and refinement of the structure

A three-dimensional Patterson synthesis was computed with a computer program by Fritchie & Guggenberger (1967). The metal atoms were found through interpretation of the Patterson function and the oxygen atoms were located on difference Fourier maps. The structure was refined with a full-matrix least-squares program by Finger (1969). Atomic scattering factors for neutral atoms were taken from Cromer & Mann (1968). They were corrected for anomalous dispersion (Cromer, 1965). The function minimized was $\sum w_i(KF_o - |F_c|)^2$ where w_i is the weight based on counting statistics and K a scale factor. Because of the rapid quenching described above, the crystal was close to 'ideally imperfect' in its mosaic character and no extinction correction was made. As a check for absolute configuration, least-squares refinements were carried out whereby the indices hkl were changed to $\bar{h}\bar{k}\bar{l}$. The resulting conventional R value was 0·047 as compared with 0·036 for the correct configuration. Both values correspond to refinements with isotropic thermal parameters. Reflections where F_o was less than three standard deviations were given zero weight in the refinements and are marked with an asterisk in the list of observed and calculated structure factors (Table 2).

Table 2. *Observed and calculated structure factors of β*-$SnWO_4$

The columns contain the values h, k, F_{obs}, F_{calc}. Reflections with zero weight in the least squares refinement are marked with an asterisk.

L = 0			
0	0	614	616
2	0	213	219
4	0	195	197
6	0	251	260
8	0	67	61
10	0	106	106
12	0	100	98
1	1	47	47
2	1	304	320
1	2	60	59
3	1	30	31
1	3	42	42
4	1	231	234
1	4	40	39
5	1	25	26
1	5	32	33
6	1	55	55
1	6	9	7*
7	1	18	25*
1	7	22	25*
8	1	158	160
1	8	27	28*
9	1	21	5*
1	9	58	59
10	1	85	84
1	10	18	25*
11	1	20	18*
1	11	28	27*
12	1	40	31
1	12	0	5*
2	2	77	75
3	2	71	72
2	3	14	16*
4	2	106	105
2	4	67	67
5	2	58	56
2	5	220	221
6	2	121	121
2	6	111	110
7	2	0	11*
2	7	18	14*
8	2	24	27*
2	8	37	35
9	2	50	51
2	9	38	37
10	2	40	45
2	10	48	44
11	2	22	25*
2	11	108	108
12	2	40	43*
2	12	31	43*
3	3	11	8*
4	3	33	34
3	4	77	74
5	3	67	67
3	5	15	1*
6	3	12	5*
3	6	18	21*
7	3	56	60
3	7	0	5*
8	3	0	7*
3	8	48	50
9	3	0	10*
3	9	0	4*
10	3	0	8*
3	10	51	53
11	3	36	38
3	11	12	4*
4	4	91	90
5	4	41	47
4	5	184	185
6	4	126	128
4	6	127	126
7	4	23	20*
4	7	121	116
8	4	37	35
4	8	30	27
9	4	52	53
4	9	33	36*
10	4	60	56
4	10	55	54
11	4	38	29
4	11	87	90
5	5	27	29
6	5	34	36
5	6	18	12*
7	5	33	33
5	7	29	25*
8	5	143	142
5	8	23	27*
9	5	0	1*
5	9	46	44
10	5	85	83
5	10	9	24*
11	5	16	22*
5	11	8	25*
6	6	177	180
7	6	0	0*
6	7	18	18*
8	6	48	47
6	8	41	43
9	6	29	2*
6	9	0	4*
10	6	82	79
6	10	79	77
7	7	20	20*
8	7	93	95
7	8	21	15*
9	7	17	7*
7	9	48	47
10	7	52	54
7	10	20	19*
8	8	3	12*
9	8	37	34*
8	9	18	27*
L = 1			
1	1	100	95
2	1	158	154
3	1	98	95
4	1	133	132
5	1	62	60
6	1	42	39
7	1	69	73
8	1	81	82
9	1	45	46
10	1	46	51
11	1	37	27
12	1	28	21*
2	2	107	107
3	2	43	40
2	3	270	274
2	4	92	93
4	2	149	146
5	2	124	125
2	5	95	94
6	2	183	186
2	6	40	37
7	2	74	78
2	7	101	101
8	2	48	47
2	8	71	70
9	2	41	33
2	9	119	120
10	2	84	80
2	10	42	37
11	2	60	57
2	11	24	25*
12	2	75	75
2	12	16	23*
3	3	168	166
4	3	223	223
3	4	30	27
5	3	53	52
3	5	48	50
6	3	30	32
3	6	61	62
7	3	68	68
3	7	81	76
8	3	141	141
3	8	39	37
9	3	70	78
3	9	85	82
10	3	82	81
3	10	0	15*
11	3	25	14*
3	11	0	15*
4	4	114	111
5	4	91	91
4	5	65	63
6	4	143	142
4	6	31	32
7	4	65	66
4	7	95	92
8	4	20	29*
4	8	83	83
9	4	28	24*
4	9	98	97
10	4	69	69
4	10	47	48
11	4	49	45
4	11	0	17*
5	5	38	47
6	5	28	23
5	6	34	39
7	5	41	41
5	7	51	48
8	5	55	51
5	8	83	79
9	5	31	30*
5	9	25	26*
10	5	28	25*
5	10	41	43
11	5	19	25*
5	11	32	24*
6	6	25	20*
7	6	26	20*
6	7	16	30*
8	6	27	24*
6	8	119	118
9	6	50	46
6	9	9	19*
10	6	17	23*
6	10	67	66
7	7	55	58
8	7	76	79
7	8	52	52
9	7	30	37*
7	9	35	40*
10	7	43	42
7	10	36	31
8	8	32	34*
9	8	28	28*
8	9	86	85
L = 2			
2	2	58	57
3	2	46	43
4	2	59	59
5	2	107	105
6	2	48	48
7	2	67	68
8	2	35	35
9	2	25	30*
10	2	34	40*
11	2	42	48
12	2	15	18*
3	3	35	30
4	3	42	41
3	4	53	55
5	3	40	47
3	5	211	215
6	3	64	64
3	6	24	25*
7	3	36	31
3	7	140	141
8	3	36	36
3	8	20	22*
9	3	20	8*
3	9	36	31
10	3	7	14*
3	10	26	26*
11	3	22	21*
3	11	99	99
4	4	57	59
5	4	122	124
4	5	90	89
6	4	59	57
4	6	59	60
7	4	71	74
4	7	48	46
8	4	49	44
4	8	40	42
9	4	41	35
4	9	23	27*
10	4	44	43
4	10	40	40
11	4	55	58
4	11	40	42
5	5	64	65
6	5	40	39
5	6	163	161
7	5	102	102
5	7	47	51
8	5	60	64
5	8	39	40
9	5	112	111
5	9	33	21
10	5	33	37*
5	10	74	70
11	5	32	23*
5	11	32	33*
6	6	80	79
7	6	109	107
6	7	5	23*
8	6	19	19*
6	8	18	21*
9	6	8	28*
6	9	27	40*
10	6	33	33*
6	10	32	34*
7	7	57	61
8	7	45	46
7	8	21	26*
9	7	76	75
7	9	39	30
8	8	15	22*
9	8	11	19*
8	9	25	23*
L = 3			
3	3	287	292
4	3	6	10*
5	3	86	87
6	3	0	1*
7	3	125	128
8	3	14	15*
9	3	138	141
10	3	0	7*
11	3	26	23*
4	4	16	26*
5	4	167	167
4	5	27	23*
6	4	9	16*
4	6	61	63
7	4	109	111
4	7	24	32*
8	4	14	27*
4	8	38	37
9	4	19	27*
4	9	29	11*
10	4	32	19*
4	10	18	13*
11	4	81	81
4	11	11	15*
5	5	20	23*
6	5	39	49
5	6	22	22*
7	5	44	45
5	7	42	45
8	5	20	26*
5	8	129	131
9	5	44	49
5	9	42	47
10	5	0	13*
5	10	78	74
6	6	17	9*
7	6	0	17*
6	7	53	53
8	6	41	42
6	8	12	10*
9	6	24	7*
6	9	0	6*
10	6	36	40
6	10	0	6*
7	7	55	57
8	7	28	27*
7	8	90	91
9	7	79	69
7	9	75	70
7	9	69	70
8	8	10	23*
L = 4			
4	4	74	76
5	4	89	87
6	4	67	68
7	4	69	68
8	4	42	40
9	4	20	24*
10	4	39	47
5	5	59	59
6	5	38	39
5	6	128	128
7	5	72	77
5	7	35	37
8	5	82	81
5	8	26	34*
9	5	85	91
5	9	23	18*
10	5	42	42
5	10	55	58
6	6	94	94
7	6	86	87
6	7	0	29*
8	6	36	25
6	8	26	23*
9	6	13	23*
6	9	44	47
10	6	40	42
6	10	41	42
7	7	42	52
8	7	44	48
9	7	59	67
7	9	33	21*
8	8	28	26*
L = 5			
5	5	22	24*
6	5	30	30
7	5	36	40
8	5	51	44
9	5	11	16*
10	5	20	28*
6	6	17	27*
7	6	29	17*
6	7	27	33*
8	6	19	23*
6	8	102	108
9	6	32	35*
6	9	0	18*
7	7	46	39
8	7	66	68
7	8	27	37*
L = 6			
6	6	134	135
7	6	7	16*
8	6	27	33*
7	7	0	20*
8	7	64	73
7	8	0	15*
L = 7			
7	7	25	45*

The final conventional R values are 0·074 (total of 391) and 0·034 (248 observed reflections). Final positional and thermal parameters are listed in Table 3.

Discussion

The structure of β-SnWO$_4$ is shown in Figs. 1 and 2. Considering the higher electropositivity of the tin atom, it may be described as an arrangement of $[WO_4]^{2-}$ tetrahedra interspersed with Sn^{2+} ions. The $[WO_4]^{2-}$ tetrahedra are not connected, *i.e.* they do not share oxygen atoms. The W, Sn, and O(1) atoms are situated on the threefold axes of the unit cell, while the O(2) atoms – in the general position – fill the remaining space.

The structure may be viewed as being rocksalt-like where the cation is Sn^{2+} and the anion is $[WO_4]^{2-}$. Structures of this type have been observed at high temperature for $A^{1+}(BF_4)$, $A^{1+}(ClO_4)$, and $A^{2+}(SO_4)$ compounds (for references see Wyckoff, 1965). In these phases the tetrahedral unit is possibly freely rotating (perfect analogy to NaCl, space group $Fm3m$). If the BX_4 tetrahedra are frozen in, a structure of lower symmetry must result. For some of the above mentioned compounds, space group $F\bar{4}3m$ has been reported with perfect tetrahedral site symmetries for the cations. The β-SnWO$_4$ structure is of still lower symmetry, caused by the 'lone pair distortion' of Sn^{2+} which will be discussed below.

Phase transitions have been reported for almost all ABX_4 phases mentioned above. The resulting low-temperature structure has not always been well characterized. In most cases it was reported isotypic with the orthorhombic $BaSO_4$ structure (Wyckoff, 1965). The β-SnWO$_4$ structure is another possibility. Our DTA data show no transition for β-SnWO$_4$ within its stable range (670 to 782 °C). It appears unlikely that the WO_4 tetrahedra rotate freely at these temperatures, if one considers that the Sn–O interaction is certainly more covalent then the A–O interaction (the A metals of the above mentioned compounds are all of the first three groups of the Periodic Table).

The space group of β-SnWO$_4$ is the same as for β-cristobalite (SiO_2), carnegieite ($NaAlSiO_4$), and Na_2CaSiO_4 (for references see Wyckoff, 1963, 1968). Like β-SnWO$_4$ these structures have oxygen atoms in the twelve- and fourfold position of T^4. The metal atoms occupy tetrahedral and more or less distorted octahedral positions. There is, however, no simple correspondence in the positional parameters of the oxygen atoms and therefore no close structural relation of β-SnWO$_4$ to the β-cristobalite family.

The $[WO_4]^{2-}$ tetrahedron in β-SnWO$_4$ is fairly regular (Table 4) suggesting almost ideal d^3s hybridization. The average W–O distance of 1·750 Å is in good agreement with the distance of about 1·77 Å calculated from the radii given by Shannon & Prewitt (1969). The

Table 3. *Final positional and thermal parameters of cubic* ($P2_13$–T^4) β-SnWO$_4$

Positional parameters are $\times 10^4$. Vibrational parameters ($\times 10^5$) of Sn and W are defined through $T=\exp(-\sum_i \sum_j h_i h_j \beta_{ij})$. Isotropic thermal parameters B of oxygen atoms are given in Å^2. Numbers in parentheses are estimated standard deviations in the least significant digits.

	Position	x	y	z	β_{11} or B	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	4(*a*)	8416 (2)	8416 (2)	8416 (2)	466 (12)	466 (12)	466 (12)	−56 (28)	−56 (28)	−56 (28)
W	4(*a*)	1644 (1)	1644 (1)	1644 (1)	332 (7)	322 (7)	322 (7)	7 (13)	7 (13)	7 (13)
O(1)	4(*a*)	3039 (16)	3039 (16)	3039 (16)	1·60 (36)					
O(2)	12(*b*)	8638 (19)	7729 (18)	5470 (18)	2·02 (23)					

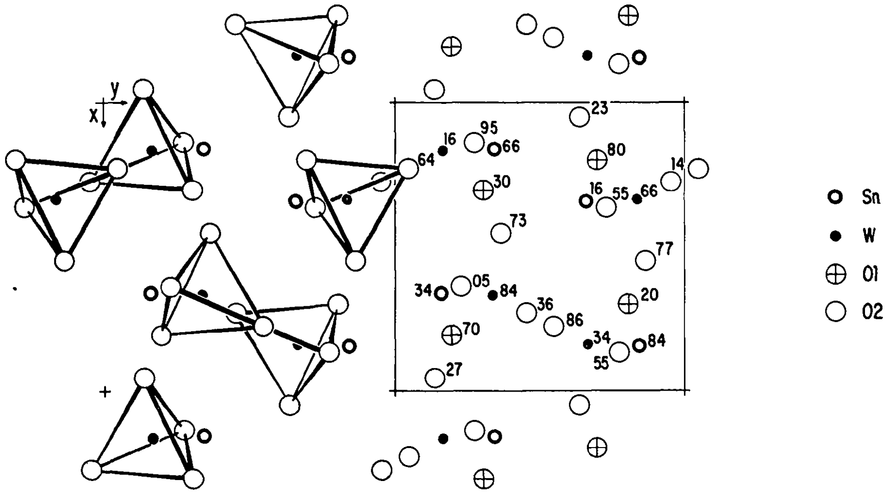

Fig. 1. Projection of the β-SnWO$_4$ structure. The $[WO_4]^{2-}$ tetrahedra are not linked. In the right hand side of the projection the z coordinates of the atoms are given in hundreths.

W–O(1) distance is slightly larger than the W–O(2) distance in accord with the higher coordination number of O(1).

Table 4. *Interatomic distances and angles in β*-SnWO$_4$

All distances shorter than 3·5 Å are given. Standard deviations were computed from e.s.d.'s of positional parameters and lattice constants. They are all less than 0·015 Å for metal–oxygen distances, 0·028 Å for oxygen–oxygen distances and 1·5° in interatomic angles.

Sn	3	O(2)	2·214 Å	O(1)–Sn–O(1)	113·6°(3×)
	3	O(1)	2·810	O(1) O(2)	75·6 (3×)
				O(1) O(2)	81·3 (3×)
W	3	O(2)	1·746	O(1) O(2)	154·1 (3×)
		O(1)	1·764	O(2) O(2)	82·4 (3×)
O(1)	3	Sn	2·810	O(1)–W–O(2)	108·4 (3×)
		W	1·764	O(2) O(2)	110·5 (3×)
	3	O(2)	2·848		
	3	O(2)	3·116		
	3	O(2)	3·304	Sn–O(1)–Sn	107·1 (3×)
				Sn W	111·7 (3×)
O(2)		Sn	2·214		
		W	1·746		
		O(1)	2·848	Sn–O(2)–W	162·2
	2	O(2)	2·870		
	2	O(2)	2·917		
		O(1)	3·116		
		O(1)	3·304		
	2	O(2)	3·385		

There are two very different kinds of oxygen in the structure. O(1) is in approximate tetrahedral coordination forming one short bond to W and three fractional bonds (2·81 Å) to tin atoms. The bond angles are close to the ideal tetrahedral angle of 109°; nevertheless the tetrahedron is far from ideal because of the differences in bond lengths. The other oxygen, O(2), forms one bond to W and one to Sn. The bond angle is 162°. As might be expected, this oxygen with the lower coordination number is the oxygen which forms the much shorter bond to tin and the slightly shorter bond to tungsten.

The tin atom has an environment characteristic for the lone pair of Sn^{2+} with close neighbors on one side only (Fig. 3). There are six oxygen atoms within bonding distance forming a distorted octahedron around the tin atom. The nonbonding electron pair may be viewed as another ligand added into one face of this octahedron. The three O(1) atoms of that face are pushed back by the negative charge of this 'ligand', and they in turn repel the three tightly bound O(2) atoms. Thus the O(2)–Sn–O(2) angle is 82°, which is less than not only the ideal tetrahedral angle (*sp*^{3} hybridization for Sn) but also the octahedral angle of 90° (*sp*^{3}*d*^{2} hybrid).

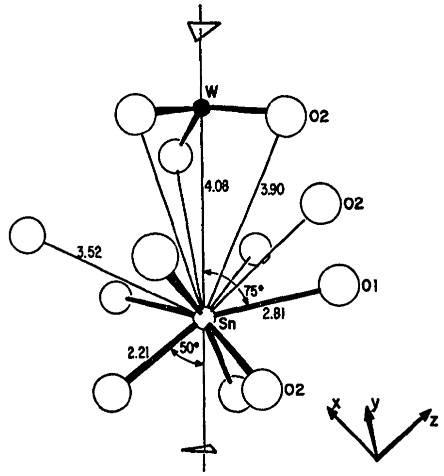

Fig. 3. Nearest neighbor environment of the Sn atom in β-SnWO$_4$.

Little information is available for divalent tin in other solid state compounds (Rundle & Olson, 1964; Donaldson, 1967). Few compounds have been prepared, and not all structures have been determined. Of the known structures with distorted Sn^{2+} environment, three short bonds at one side of the tin atom were also found in SnF$_2$, NaSn$_2$F$_5$, SnCl$_2$, KSnCl$_4$.H$_2$O, SnSO$_4$, SnS, and low-temperature SnSe. On the other hand, in SnTe and high-temperature SnSe the Sn atom has undistorted octahedral environment. For Pb^{2+} symmetric configurations occur more frequently. PbO, like SnO, has a distorted NaCl structure (Moore & Pauling, 1941) while Pb^{2+} in PbWO$_4$ with scheelite structure (Sillén & Nylander, 1943; Plakhov, Pobedimskaya, Simonov & Belov, 1971) is highly symmetric. Thus [WO$_4$]$^{2-}$ differentiates between Sn^{2+} and Pb^{2+} in a similar way as does S^{2-}: SnS and β-SnWO$_4$ show the lone pair effect for Sn^{2+}, while the environment of Pb^{2+} in PbS and PbWO$_4$ (scheelite) is symmetric, *i.e.* the lone pair resides in the *s* orbital.

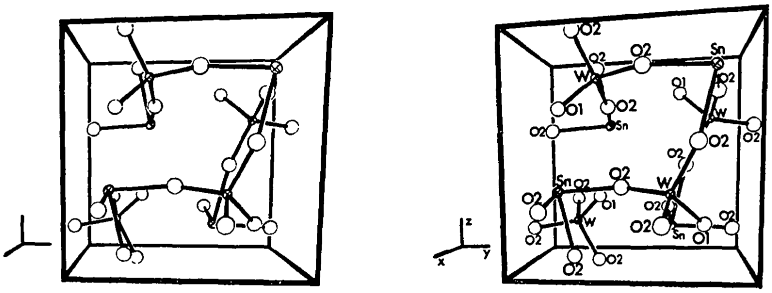

Fig. 2. Stereodiagram of β-SnWO$_4$.

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The Crystal and Molecular Structure of Uranyl Oxalate Trihydrate

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Uranyl oxalate trihydrate, $UO_2C_2O_4.3H_2O$, crystals are monoclinic with lattice parameters $a=5\cdot623$ (5), $b=17\cdot065$ (2), $c=9\cdot451$ (3) Å and $\beta=98\cdot74$ (1)°. The space group is $P2_1/C$ with $Z=4$. 513 visually estimated reflexions were corrected for absorption and the structure refined by Fourier and least-squares methods to $R=0\cdot079$. Each uranium atom exists as a linear $(O\text{–}U\text{–}O)^{2+}$ ion with five secondary oxygen atoms coordinated to it in a perpendicular plane. The average distances are $U\text{–}O_I=1\cdot63$ (4) and $U-O_{II}=2\cdot49$ (4) Å. The oxalate groups are planar and tetradentate, each bridging two uranyl ions. Only one water molecule is coordinated to the uranium atom. The structure is consistent with the thermal behaviour of the compound.

Introduction

Several oxalato complexes of dioxouranium(VI) with varying uranium to oxalate ratios are known, but no detailed structural work has been reported. The fact that an anhydrous ammonium salt of $[UO_2(C_2O_4)_3]^{4-}$ was isolated was interpreted to show that in oxalato complexes the uranyl ion requires six ligands in a plane for coordination saturation (Chernyaev, 1966). In the bisoxalatodioxouranate(VI) complexes two water molecules are assumed to complete the hexagonal arrangement. But substitution reactions on bisoxalato complexes (Shchelokov & Belomestnykh, 1969) have indicated a pentagonal coordination for the uranyl ion, which is sterically and geometrically stable in a plane (Evans, 1963). We have initiated detailed structural investigation of solid oxalate complexes by the method of single-crystal X-ray diffraction. The crystal and molecular structures of uranyl oxalate trihydrate are discussed here.

Preparation

A hot saturated solution of oxalic acid was added to a concentrated solution of pure uranyl nitrate in $1\cdot0M$ nitric acid at 80 °C. The crystals separated on standing and were washed with water, alcohol and ether. Chemical and thermal analysis confirmed the composition $UO_2C_2O_4.3H_2O$.