

Table 5. V–O bond lengths (Å) and V–O–V bond angles (°) in $M_2V_2O_7$ structures

	$\langle V-O_t \rangle$	$\langle V-O_i \rangle$	V–O–V
$Mn_2V_2O_7^a$	1.69	1.760	180
$Cd_2V_2O_7^b$	1.692	1.757	180
$Zn_2V_2O_7^c$	1.697	1.751	151
$\beta Cu_2V_2O_7^{d*}$	1.693	1.770	
$\alpha Cu_2V_2O_7$	1.702	1.743	147.8
$Ba_2V_2O_7^e$	1.687	1.820	123.7
	1.688	1.823	125.6
$Sr_2V_2O_7^f$	1.69	1.81	122
	1.71	1.81	124
$Pb_2V_2O_7^g$	1.692	1.817	122
$Co_2V_2O_7^h$	1.694	1.849	117.6
$Ni_2V_2O_7^h$	1.692	1.846	117.1

a Dorm & Marinder (1967). *b* Au & Calvo (1967). *c* Gopal & Calvo (1973). *d* Mercurio-Lavaud & Frit (1973*b*). *e* Hawthorne & Calvo (1975). *f* Baglio & Dann (1971). *g* Shannon & Calvo (1973). *h* Sauerbrei, Faggiani & Calvo (1974).

* The table of atomic positions in this paper seems to contain errors. The values used here are those reported by these authors.

Table 5 summarizes the average bridging and terminal V–O bond lengths and V–O–V bond angles in the series of divalent metal ion divanadates. As the V–O–V angle increases the average bridging V–O bond length, $\langle V-O_b \rangle$, decreases. The average terminal V–O bond length shows no systematic variation. All anions with V–O–V bond angles of less than 148° have strong interactions between the divalent metal ion and the bridging oxygen atom. Therefore, these structures seem to fall into two groups based upon this characteristic. In the case of $Mg_2V_2O_7$ (Gopal & Calvo, 1974) one side of the anion has a long, but significant, interaction with a fifth oxygen atom ($V-O=2.440$ Å).

Acta Cryst. (1975). B31, 605

The Crystal Structure of Tetra-(4-methylphenyl)tin

BY ANASTAS KARIPIDES AND KAREN WOLFE

Department of Chemistry, Miami University, Oxford, Ohio 45056, U.S.A.

(Received 8 August 1974; accepted 11 October 1974)

Abstract. $(4-CH_3C_6H_4)_4Sn$, tetragonal, $I\bar{4}$, $a=13.819$ (8), $c=6.406$ (4) Å, $Z=2$, $D_c=1.31$, $D_o=1.32$ g cm⁻³ (by flotation in aqueous KI solution). The structure consists of discrete molecules which have crystallographic $\bar{4}$ symmetry. The methyl group is rigidly involved in the intermolecular structure. The final R value is 0.035.

Introduction. The title compound was prepared from the reaction of anhydrous tin tetrachloride and 4-methylphenylmagnesium bromide in ether/benzene solution. The purified compound was isolated from the crude reaction product by Soxhlet extraction and re-

Despite this, the structure is closely related to the thortvietite-like series of compounds. Many of these divalent metal ion divanadates show polymorphic transition. For example, Angenault (1970) has reported an orthorhombic phase of $Zn_2V_2O_7$ which is likely to be isotypic with that of $\alpha Cu_2V_2O_7$. Further studies of these polymorphs seems desirable.

This research has been supported by a grant from the National Research Council of Canada.

References

- ANGENAULT, J. (1970). *Rev. Chim. Min.* **7**, 651–699.
 AU, P. K. L. & CALVO, C. (1967). *Canad. J. Chem.* **43**, 2297–2302.
 BAGLIO, J. A. & DANN, J. N. (1971). *J. Solid State Chem.* **4**, 87–93.
 DORM, E. & MARINDER, B. (1967). *Acta Chem. Scand.* **21**, 590–591.
 GOPAL, R. & CALVO, C. (1973). *Canad. J. Chem.* **51**, 1004–1009.
 GOPAL, R. & CALVO, C. (1974). *Acta Cryst.* B30, 2491–2493.
 HAWTHORNE, F. & CALVO, C. (1975). To be published.
 MANOLESCU, D. (1974). M. Sc. Thesis, McMaster Univ. Hamilton, Ontario, Canada.
 MERCURIO-LAVAUD, D. & FRIT, B. (1973*a*). *Acta Cryst.* B29, 2737–2741.
 MERCURIO-LAVAUD, D. & FRIT, B. (1973*b*). *C. R. Acad. Sci. Paris, Ser. C*, **277**, 1101–1104.
 QUARTON, M., ANGENAULT, J. & RIMSKY, A. (1973). *Acta Cryst.* B29, 567–572.
 SAUERBREI, E. E., FAGGIANI, R. & CALVO, C. (1974). *Acta Cryst.* B30, 2907–2909.
 SHANNON, R. D. & CALVO, C. (1973). *Canad. J. Chem.* **51**, 70–76.

crystallized from benzene as long colorless glistening needles. From indexed Weissenberg photographs the systematic absences $h+k+l=2n+1$ confirmed the body-centered tetragonal lattice found by Ismailzade & Zhdanov (1953). Cell parameters were determined by a least-squares refinement of the carefully measured angular settings of 12 reflections on a Picker FACS-1 automated diffractometer. The refined values given in the abstract compare with $a=13.50$ and $c=6.36$ Å reported by Ismailzade & Zhdanov (1953).

Three-dimensional intensity data were collected on the same diffractometer with zirconium-filtered $Mo K\alpha$ ($\lambda=0.71069$ Å) radiation. The details of the data col-

Table 1. *Positional and thermal parameters* ($\times 10^4$)

The thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sn	0	0	0	36 (2)	36 (2)	218 (2)	0	0	0
C(1)	327 (4)	1265 (4)	1814 (10)	43 (3)	42 (2)	219 (18)	3 (3)	-6 (7)	13 (7)
C(2)	1145 (4)	1818 (5)	1353 (12)	51 (4)	62 (4)	287 (21)	-11 (3)	24 (8)	-30 (8)
C(3)	1372 (5)	2641 (5)	2506 (16)	57 (4)	68 (5)	441 (29)	-19 (4)	26 (10)	-36 (11)
C(4)	805 (5)	2950 (5)	4164 (12)	64 (4)	55 (4)	349 (27)	3 (4)	-9 (8)	-38 (8)
C(5)	-10 (5)	2398 (5)	4650 (27)	56 (3)	65 (4)	375 (56)	9 (3)	3 (12)	-11 (12)
C(6)	-244 (4)	1588 (5)	3459 (12)	49 (4)	55 (4)	291 (21)	-1 (3)	-2 (8)	1 (8)
C(7)	1061 (6)	3845 (6)	5396 (31)	88 (5)	95 (6)	632 (81)	-5 (4)	12 (17)	-127 (23)

Table 1 (*cont.*)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(2)	1608	1603	77	4.6
H(3)	2010	3050	2100	5.6
H(5)	-465	2600	5945	4.6
H(6)	-897	1194	3829	4.2
H(7A)	582	4432	4973	8.0
H(7B)	1792	4062	5027	8.0
H(7C)	1009	3708	7048	8.0

lection have been previously described (Karipides, Forman, Thomas & Reed, 1974). The crystal had approximate dimensions $0.13 \times 0.14 \times 0.26$ mm and was mounted along the longest dimension (*c*). 645 independent reflections out to 50° in 2θ were measured in the θ - 2θ scan mode. All reflections collected had $I > \sigma(I)$ and all were retained for use in the structure determination and refinement.

The space group $I\bar{4}$ was initially assumed and subsequently verified by the complete solution of the structure. The crystallographic symmetry requires the tin atom to be at the origin. The non-hydrogen atoms in the one independent 4-methylphenyl group were found from a difference Fourier map phased by the tin atom. After a convergent isotropic refinement using the tin and carbon atoms the ring hydrogen atoms were introduced by placing them in theoretical positions assuming the C-H bond (length fixed at 1.08 Å) bisects the calculated C-C-C angle. The locations of the methyl hydrogen atoms were determined from a difference electron density map and repositioned at the experimentally observed orientation so that the C-H lengths equaled 1.08 Å. All hydrogen atoms were assigned the isotropic temperature factors of the carbon atoms to which they were attached.

The structure was refined by full-matrix least-squares calculations assuming anisotropic motion for the tin

and carbon atoms. The hydrogen atom parameters were not varied. The quantity minimized was $\sum \omega(|F_o| - |F_c|)^2$ where the weight applied to each observation was taken to be $1/\sigma^2(F)$ where $\sigma(F)$ was determined as described previously (Karipides, Forman, Thomas & Reed, 1974). New hydrogen positions were calculated after each least-squares run. The final refinement resulted in a conventional *R* value, $\sum(|F_o| - |F_c|)/\sum|F_o|$, of 0.035 and a weighted *R* value, $[\sum \omega(|F_o| - |F_c|)^2 / \sum \omega|F_o|^2]^{1/2}$, of 0.036. The final standard deviation in an observation of unit weight was 1.13.

The atomic scattering factors for neutral tin (corrected for $\Delta f'$ and $\Delta f''$) and carbon were taken from Cromer & Waber (1965) and Cromer (1965). The hydrogen atom scattering factors were those of Stewart, Davidson & Simpson (1965). In addition to local programs for the IBM 370/165 computer, the following programs or modifications were used: *FORDAP* (Zalkin, 1974, unpublished), *ORFLS* and *ORFFE* (Busing, Martin & Levy, 1962, 1964), *ORTEP* (Johnson, 1965), *PLANET* (Smith, 1962). The final atomic positional and thermal parameters and their standard deviations are given in Table 1.*

Discussion. The structure of tetra-(4-methylphenyl)tin was carried out to obtain an accurate description of the role of the methyl group in the molecular packing and the conformation of the aryl ring (Karipides, Forman, Thomas & Reed, 1974). A qualitative two-dimensional structure of the title compound based on

* The table of structure factors ($10|F_o|$ and $10|F_c|$) has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30724 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Bond distances* (Å) *and valence angles* ($^\circ$)

Sn—C(1)	2.147 (6)	C(3)—C(4)	1.387 (11)
C(1)—C(2)	1.396 (8)	C(4)—C(5)	1.395 (10)
C(1)—C(6)	1.390 (9)	C(5)—C(6)	1.392 (12)
C(2)—C(3)	1.392 (10)	C(4)—C(7)	1.510 (13)
C(1)—Sn—C(1) ($\bar{x}\bar{y}z$)	114.4 (3)	C(1)—C(6)—C(5)	122.8 (7)
C(1)—Sn—C(1) ($y\bar{x}\bar{z}$)	107.0 (2)	C(3)—C(4)—C(7)	121.3 (8)
C(6)—C(1)—C(2)	116.4 (6)	C(5)—C(4)—C(7)	121.4 (9)
C(1)—C(2)—C(3)	121.8 (4)	H(7A)—C(7)—H(7B)	107.9 (10)
C(2)—C(3)—C(4)	122.0 (6)	H(7A)—C(7)—H(7C)	109.7 (12)
C(3)—C(4)—C(5)	117.3 (8)	H(7B)—C(7)—H(7C)	109.1 (12)
C(4)—C(5)—C(6)	120.3 (11)		

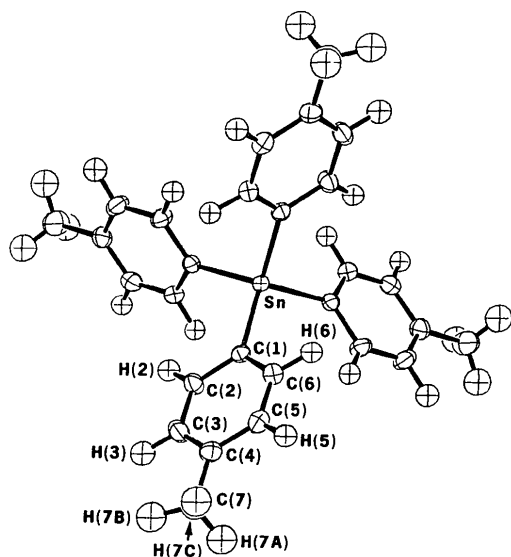


Fig. 1. A view of $(4\text{-CH}_3\text{C}_6\text{H}_4)_4\text{Sn}$ along the molecular $\bar{4}$ axis.

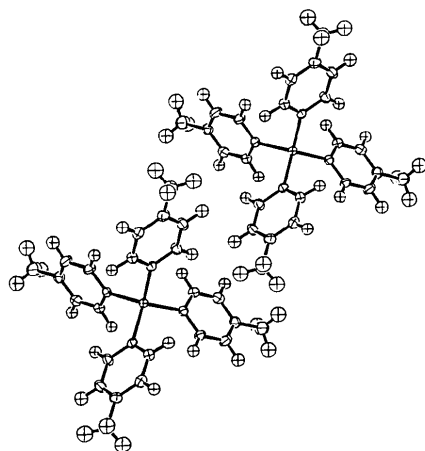


Fig. 2. A projection on the ab plane of the $(4\text{-CH}_3\text{C}_6\text{H}_4)_4\text{Sn}$ unit cell.

only 58 $hk0$ reflections has been reported (Ismailzade & Zhdanov, 1953), but in that account the atom z coordinates and, hence, the details of the structure were not determined.

Interatomic distances and angles are given in Table 2. A view of the molecular structure and the atom-numbering scheme are presented in Fig. 1. The projection of the unit cell on the ab plane is shown in Fig. 2.

The structure consists of discrete molecules with crystallographically imposed $\bar{4}$ symmetry. The observed Sn–C(1) length, 2.147 (6) Å, compares well with the 2.14 (1) Å found in tetraphenyltin (Chieh & Trotter, 1970; Akmed and Aleksandrov, 1970) and 2.126 (8) Å in tetrakis(pentafluorophenyl)tin (Karipides, Forman, Thomas & Reed, 1974). The aryl–methyl bond distance, C(4)–C(7), is 1.510 (3) Å, in agreement with typical

values previously observed (Baenziger & Schultz, 1973). The aryl ring is planar; the equation of the unit-weighted least-squares plane fitted to the seven carbon atoms is $-0.5411X + 0.5617Y - 0.6259Z - 0.0155 = 0$. The average deviation of the seven carbon atoms from this plane is 0.009 Å with the largest being 0.013 Å. The tin atom is also in this plane (-0.008 Å displacement). However, the phenyl ring does deviate substantially from idealized D_{6h} symmetry in a manner that has been previously documented for similarly bonded aryl groups (Churchill & Veidis, 1972; Churchill & Kalra, 1974).

The 4-methylphenyl ring plane makes an angle of 51.2° with the xy plane which compares to 44° estimated by Ismailzade & Zhdanov (1953). The plane formed by the atoms H(7A)–C(7)–C(4) makes an angle of 74.8° with the planar aryl ring which along with the dihedral angles H(7A)–C(7)–C(4)–H(7C), 121.3° , H(7C)–C(7)–C(4)–H(7B), 120.3° , H(7B)–C(7)–C(4)–H(7A), 118.4° specifies the orientation of the methyl group.

The crystal structure can be expressed succinctly in terms of the angular parameters previously defined (Karipides, Forman, Thomas & Reed, 1974). The rotation (φ) of the molecule about the c axis measured from the a axis is -14.5° while the rotation (α) of the aryl ring plane about the Sn–C bond axis measured from a vertical plane through z is 49.3° . The C(1)–Sn–C(1) ($\bar{x}\bar{y}z$) valency angle (θ) is 114.4° . The crystal packing differs from that found in tetraphenyltin which crystallizes in space group $P\bar{4}2_1c$ and has $\varphi = 7.4^\circ$, $\alpha = 57.5^\circ$ and $\theta = 110.8^\circ$. The difference in packing is due to the extensive involvement of the methyl group in the intermolecular structure of the crystal. All three methyl hydrogen atoms [especially H(7A)] are involved in close H...H interactions and are: H(7A)...H(7A) ($\bar{x}, 1-y, z$), 2.25 Å; H(7B)...H(5) ($\frac{1}{2}-y, \frac{1}{2}-x, \frac{3}{2}-z$), 2.79 Å; H(7C)...H(5) ($\frac{1}{2}-y, \frac{1}{2}-x, \frac{3}{2}-z$), 2.58 Å. In comparison the shortest H...H distances not involving methyl hydrogen atoms are H(2)...H(6) (y, \bar{x}, \bar{z}), 2.75 Å; H(3)...H(2) ($\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$), 2.74 Å. The shortest C...H non-bonded distance is C(6)...H(6) ($y, \bar{x}, 1-z$), 2.81 Å. These close contacts involving the methyl hydrogens require the methyl group to be rigidly oriented in the lattice.

Grateful acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society and the Miami University Undergraduate Research Committee for support of this work. We thank Mr R. H. P. Thomas for preparation of the compound.

References

- AKMED, N. A. & ALEKSANDROV, G. G. (1970). *Zh. Strukt. Khim.* **11**, 891–894.
 BAENZIGER, N. C. & SCHULTZ, R. J. (1973). *Acta Cryst.* **B29**, 337–344.

- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Oak Ridge National Laboratory Report ORNL-TM-305.
- BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1964). *ORFFE*. Oak Ridge National Laboratory Report ORNL-TM-306.
- CHIEH, P. C. & TROTTER, J. (1970). *J. Chem. Soc. (A)*, pp. 911–914.
- CHURCHILL, M. R. & KALRA, K. L. (1974). *Inorg. Chem.* **13**, 1065–1071.
- CHURCHILL, M. R. & VEIDIS, M. V. (1972). *J. Chem. Soc. Dalton*, pp. 670–675.
- CROMER, D. T. (1965). *Acta Cryst.* **18**, 17–23.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- ISMAILZADE, I. G. & ZHDANOV, G. S. (1953). *Zh. Fiz. Khim.* **27**, 550–553.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794 (revised, 1970).
- KARIPIDES, A., FORMAN, C., THOMAS, R. H. P. & REED, A. T. (1974). *Inorg. Chem.* **13**, 811–815.
- SMITH, D. L. (1962). *PLANET*. Ph.D. Thesis, Univ. of Wisconsin, Madison, Wisconsin.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1975). **B31**, 608

Zr₁₄Cu₅₁ and Hf₁₄Cu₅₁ with GdAg_{3.6} Structure Type

BY J. -P. GABATHULER, P. WHITE AND E. PARTHÉ

*Laboratoire de Cristallographie aux Rayons X de l'Université de Genève,
32 Bd d'Yvroy, CH-1211 Genève 4, Switzerland*

(Received 24 September 1974; accepted 11 October 1974)

Abstract. Hf₁₄Cu₅₁, hexagonal, *P6/m* (No. 175), $a = 11.18$ (1), $c = 8.235$ (5) Å, $U = 1782.8$ Å³, $Z = 1$, F.W. 5739.4, $D_x = 10.69$ g cm⁻³, $F(000) = 2487$. Counter technique, absorption correction, direct methods, least-squares refinement. $R = 0.085$ for 568 reflexions. Zr₁₄Cu₅₁ ($a = 11.25$ (1), $c = 8.275$ (10) Å) and Hf₁₄Cu₅₁ are isotopic with GdAg_{3.6}.

Introduction. In the Cu-rich part of the system Hf–Cu the phases HfCu₄ and HfCu₅ of unknown structure have been reported recently by Perry (1974). Phases of the same composition were found in the system Zr–Cu (Perry & Hugi, 1972).

Samples of composition HfCu₄ and ZrCu₄ were prepared by arc melting the component elements under purified argon atmosphere (Hf 99.9%, Zr 99.9%, Cu 99.999%). The alloying of Cu with Hf or Zr leads to an appreciable increase in hardness. It was possible to isolate small single crystals of ZrCu_{~4} and HfCu_{~4} (~40 μm diameter). Precession and Weissenberg photographs showed that the two compounds, later to be described by the formulae Zr₁₄Cu₅₁ and Hf₁₄Cu₅₁, were isotopic and that they crystallized with a hexagonal cell with Zr₁₄Cu₅₁: $a = 11.25$ (1), $c = 8.275$ (10) Å; Hf₁₄Cu₅₁: $a = 11.18$ (1), $c = 8.235$ (5) Å.

As there were no systematic extinctions and the crystals show low hexagonal Laue symmetry, the possible space groups were *P6*, *P6̄* and *P6/m*.

A structure analysis was performed on the HfCu_{~4} single crystal. 568 non-equivalent intensities were measured on a Philips four-circle automatic diffractometer with graphite-monochromatized Mo *K*α radiation. Correction for absorption [$\mu(\text{Hf}_{14}\text{Cu}_{51}) = 734 \text{ cm}^{-1}$] was made (de Meulenaer & Tompa, 1965). The structure was

solved by direct methods with the program *LSAM* (Main, Woolfson & Germain, 1972). The *E* map showed that the proper space group was *P6/m*, and it also allowed 14 Hf atoms and 48 Cu atoms to be located. A Fourier map showed three further Cu atoms distributed at random over six sites. The true composition of this compound is therefore Hf₁₄Cu₅₁ with a calculated density of 10.69 g cm⁻³. The final positional parameters refined after applying anomalous dispersion corrections (*International Tables for X-ray Crystallography*, 1968) and using the least-squares program in the X-RAY system (1972) are given in Table 1.* The scattering factors have been generated with analytical

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30719 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. Positional parameters for Hf₁₄Cu₅₁ with GdAg_{3.6} structure type.

Space group *P6/m* (No. 175). The temperature factor is given by the equation $T = \exp[-2\pi^2 \cdot 10^{-2} U (2 \sin \theta / \lambda)^2]$.

		<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> [Å ²]
2Hf(1)	2(<i>e</i>)	0	0	0.3114 (7)	0.2 (1)
6Hf(2)	6(<i>j</i>)	0.1138 (4)	0.3893 (4)	0	0.7 (1)
6Hf(3)	6(<i>k</i>)	0.4712 (3)	0.1417 (3)	$\frac{1}{2}$	0.4 (1)
2Cu(1)	2(<i>c</i>)	$\frac{1}{2}$	$\frac{2}{3}$	0	0.7 (4)
4Cu(2)	4(<i>h</i>)	$\frac{1}{2}$	$\frac{2}{3}$	0.2931 (14)	0.3 (2)
6Cu(3)	6(<i>k</i>)	0.0611 (10)	0.2403 (9)	$\frac{1}{2}$	0.2 (2)
12Cu(4)	12(<i>l</i>)	0.1914 (7)	0.2651 (7)	0.2365 (8)	0.7 (2)
12Cu(5)	12(<i>l</i>)	0.4942 (7)	0.1163 (7)	0.1520 (8)	0.5 (1)
12Cu(6)	12(<i>l</i>)	0.1044 (6)	0.4373 (6)	0.3296 (8)	0.4 (1)
3Cu(7)	6(<i>i</i>)	0.1146 (26)	0.1352 (26)	0	1.9 (5)