

## Note on the Crystal Structure of $T\text{-Nb}_2\text{O}_5$ and of an Isostructural High-Temperature Zr-Nb-oxide

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$T\text{-Nb}_2\text{O}_5$  was first reported by Brauer,<sup>1</sup> in his original work on the oxides of niobium. According to Brauer,  $T\text{-Nb}_2\text{O}_5$  is stable in the approximate range 500–900°C. Schäfer, Gruehn and Schulte<sup>2</sup> have prepared  $T\text{-Nb}_2\text{O}_5$  at temperatures between 400 and 800°C using, among other methods, a chemical transport reaction. In the paper of Schäfer *et al.* a summary of unit cell data previously reported is given.

In our investigation of the  $\text{ZrO}_2\text{-Nb}_2\text{O}_5$ -system<sup>3</sup> we have observed a mixed Zr-Nb-oxide isostructural with  $T\text{-Nb}_2\text{O}_5$ . This phase is formed when samples containing 8–30 mol %  $\text{ZrO}_2$  are melted at 1500°C and quenched. In a sample containing 8.5 mol %  $\text{ZrO}_2$  we obtained a single crystal of the Zr-Nb-oxide which was suitable for single crystal work. Using Weissenberg photographs,  $hk0-hk3$ , of this crystal, it was possible to index a Guinier powder photograph of the sample in detail, and thus to obtain accurate values of the unit cell dimensions. The cell parameters of the orthorhombic unit cell were refined on an IBM 360/65 computer using a program written by Lindqvist and Wengelin.<sup>4</sup> Unit cell dimensions, observed and calculated  $\sin^2\theta$  and  $d$ -values are given in Table 1. The following conditions of reflection were observed:  $hkl$ : no conditions,  $0kl$ :  $k=2n$ , and  $h0l$ :  $h=2n$ . This is characteristic for space groups  $Pba2$  (No. 32) and  $Pbam$  (No. 55).

Table 1. Crystallographic data for the Zr-Nb-oxide. Unit cell dimensions:  $a=(6.173\pm 0.003)$  Å,  $b=(29.27\pm 0.02)$  Å and  $c=(3.934\pm 0.002)$  Å. Systematically absent reflections:  $h0l$  with  $h=2n+1$ ;  $0kl$  with  $k=2n+1$ . Possible space groups:  $Pba2$  and  $Pbam$ . Powder pattern data.  $\text{CuK}\alpha_1$  radiation.  $\lambda(\text{CuK}\alpha_1)=1.54051$  Å.

$I$ obs	$\sin^2\theta \times 10^5$ obs	$d$ obs	$hkl$	$\sin^2\theta \times 10^5$ calc	$d$ calc
m	2172	5.226	1 3 0	2180	5.217
vs	3828	3.937	0 0 1	3833	3.934
m	5995	3.145	1 8 0	5997	3.145
vs	6235	3.085	2 0 0	6227	3.087
w	7948	2.732	2 5 0	7959	2.730
vs	9838	2.456	1 8 1	9822	2.458
s	10055	2.429	2 0 1	10061	2.428
w	13241	2.117	1 13 0	13260	2.115
vw	14271	2.039	3 2 0	14289	2.038
m	14641	2.013	3 3 0	14635	2.013
vs	15343	1.966	0 0 2	15333	1.967
w	17082	1.864	1 13 1	17094	1.863
s	17742	1.829	0 16 0	17729	1.829
s	18455	1.793	{ 2 11 1	18440	1.794
			{ 3 8 0	18444	1.794
vs	21327	1.668	1 8 2	21322	1.668
s	21558	1.659	0 16 1	21562	1.659
s	22262	1.632	0 10 2	22258	1.633
w	24913	1.543	4 0 0	24909	1.543
s	27780	1.461	2 16 1	27789	1.461
vvw	28732	1.434	4 0 1	28743	1.437
w	30447	1.396	3 4 2	30452	1.396
s	33057	1.340	0 16 2	33061	1.340
s	33754	1.326	3 8 2	33776	1.325

Table 2. Crystallographic data for  $T\text{-Nb}_2\text{O}_5$ . Unit cell dimensions:  $a = (6.170 \pm 0.006)$  Å,  $b = (29.25 \pm 0.03)$  Å and  $c = (3.928 \pm 0.005)$  Å. Powder pattern data.  $\text{CuK}\alpha_1$ -radiation.  $\lambda(\text{CuK}\alpha_1) = 1.54051$  Å.

$I$ obs	$\sin^2 \theta \times 10^5$ obs	$d$ obs	$h k l$	$\sin^2 \theta \times 10^5$ calc	$d$ calc
w	2174	5.224	1 3 0	2182	5.214
vs	3840	3.931	0 0 1	3845	3.928
m	5992	3.147	1 8 0	5997	3.145
vs	6220	3.088	2 0 0	6234	3.085
vw	7942	2.733	2 5 0	7968	2.729
s	9839	2.456	1 8 1	9842	2.455
m	10058	2.429	2 0 1	10079	2.426
w	13254	2.115	1 13 0	13268	2.114
w	14650	2.012	3 3 0	14650	2.012
s	15370	1.965	0 0 2	15380	1.964
w	17738	1.829	0 16 0	17753	1.828
m	18445	1.793	2 11 1	18440	1.794
			3 8 0	18464	1.793
m	21361	1.663	1 8 2	21377	1.666
m	21589	1.658	0 16 1	21598	1.657
m	22299	1.631	0 10 2	22315	1.631
vw	24935	1.542	4 0 0	24936	1.542
s	27790	1.461	2 16 1	27831	1.460

Guinier photographs of a sample of  $T\text{-Nb}_2\text{O}_5$ , kindly placed at our disposal by Professor Gruehn, are very similar to those of the Zr-Nb-oxide. Unfortunately, we have not been able to find any single crystals in the  $T\text{-Nb}_2\text{O}_5$ -sample suitable for Weissenberg investigations. Due to the great similarity between the two phases, we have, however, used the same indexing for  $T\text{-Nb}_2\text{O}_5$  as for the Zr-Nb-oxide. Unit cell dimensions, observed and calculated  $\sin^2 \theta$ - and  $d$ -values are given in Table 2. When comparing the powder pattern data for the two phases, it should be noted that all reflections from  $T\text{-Nb}_2\text{O}_5$  were diffuse and some observed reflections have been omitted because no accurate value of  $\sin^2 \theta$  could be determined.

A comparison with other published investigations of  $T\text{-Nb}_2\text{O}_5$  shows that the values of the  $a$ - and  $c$ -axes,  $a = 6.17 - 6.24$  Å and  $c = 3.92 - 3.94$  Å,<sup>6-7</sup> are in good agreement with our data. The  $b$ -value of 3.65 Å<sup>6,7</sup> is, however, about 1/8 of our value of 29.25 Å. This could be explained by the occurrence of a superstructure for  $T\text{-Nb}_2\text{O}_5$ , leading to a multiplication of the  $b$ -axis by eight, which could not be ob-

served in the powder photographs. The value  $b = 43.79$  Å<sup>6</sup> cannot be explained by our data.

The Weissenberg photographs  $hk0 - hk3$  of a single crystal of the Zr-Nb-oxide were found to be identical, with due regard to experimental errors and for the effect of thermal motion. This indicates that all the metal atoms are situated in the same plane perpendicular to the  $c$ -axis.

A two-dimensional Patterson summation  $P(u,v,p)$  based on the  $hk0$ -reflections was undertaken. The largest peaks were situated in rows parallel to the  $v$  axis with  $u = 0.0$  and  $u = 0.5$ . This indicates that all the metal atoms are situated in rows parallel to the  $b$ -axis. The intermetallic distance is 3.66 Å, *i.e.* very close to the values for the  $b$  axis reported by Holser<sup>6</sup> and Terao.<sup>7</sup>

We intend to continue the investigation in order to solve the structure in detail.

The authors thank Professor G. Lundgren for valuable discussions and Dr. S. Jagner for revising the English text. This investigation forms part of a research program supported by the Swedish Natural Science Research Council.

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Received November 3, 1972.

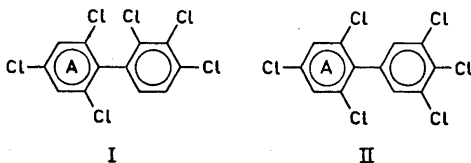
### Polychlorinated Biphenyls III.\* Synthesis of Two <sup>14</sup>C-Labelled Hexachlorobiphenyls

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Polychlorinated biphenyls (PCB) which find use, *e.g.*, in the electrical industry, are complex mixtures of compounds with one to ten chlorine atoms per molecule.<sup>2,3</sup> Their occurrence in fish and wildlife from various parts of the world has recently been the subject of comprehensive reviews.<sup>4,5</sup>

We recently reported a synthesis of two <sup>14</sup>C-tetrachlorobiphenyls.<sup>6</sup> In the present communication the synthesis of a mixture of 2,2',3,4,4',6'-hexachlorobiphenyl (I) and 2,3',4,4',5',6-hexachlorobiphenyl (II), labelled in the A rings with a specific activity of *ca.* 25 Ci/mol is described. These



\* Part II, Ref. 1.

compounds were required for current investigations into the distribution and excretion of PCB in mice and quails.<sup>7-9</sup>

Chlorination with sodium chlorate in hydrochloric acid<sup>10</sup> of uniformly labelled acetanilide-<sup>14</sup>C afforded 2,4,6-trichloroacetanilide-<sup>14</sup>C. This was hydrolysed and the 2,4,6-trichloroaniline-<sup>14</sup>C produced was used in the arylation of 1,2,3-trichlorobenzene following the general procedure described by Cadogan.<sup>11</sup> The biphenyl mixture obtained contained the labelled isomers I and II in the approximate ratio 2:1 (GLC), chromatographically indistinguishable from the two main components formed in the same coupling reaction using unlabelled 2,4,6-trichloroaniline.

The latter products were isolated in a pure state by chromatography on a silica gel column. Based on their relative retention times by GLC (*cf.* Ref. 2), the major and minor components were formulated as 2,2',3,4,4',6'-hexachlorobiphenyl (I) and 2,3',4,4',5',6-hexachlorobiphenyl (II), respectively. The structural assignments were confirmed by UV spectrometry. Compound I gives a distinct long-wave band (about 270–280 nm), similar to that produced by 2,2',3,6'-tetrachlorobiphenyl.<sup>1</sup> By comparison, compound II, similarly to 2',3,4,6'-tetrachlorobiphenyl, exhibits a shoulder only in this region.<sup>1</sup> This spectral difference, which has previously been found also in the spectra of 2,2',6-trimethylbiphenyl and 2,6-dimethylbiphenyl has been interpreted as indicating a progressive disappearance of the conjugation band about 230 nm with an increasing number of *ortho*-substituents.<sup>12</sup>

Final confirmation of the assigned structures was provided by the 100 MHz NMR spectra of the two compounds.<sup>3</sup>

*Experimental.* Activities were measured with a Packard Tri-carb model 3320 liquid scintillation spectrometer. UV-spectra were measured on a Perkin-Elmer 124 spectrophotometer. Melting points were determined on a Kofler micro hot stage. Mass spectra were recorded on an LKB 9000 spectrometer. NMR spectra were obtained on a Varian HA-100 instrument with tetramethylsilane as internal standard. All reagents used were of analytical grade unless otherwise stated.

*Gas chromatography.* The hexachlorobiphenyls were characterised by GLC using a Varian 1400 instrument fitted with an electron capture detector. Glass columns (0.18 × 160 cm) containing 4% (w/w) SF 96 on Chromosorb W A/W DMCS (100–120 mesh) at 173°