reversible. The role of benzimidazole or imidazole in the complexing of O_2 could be explained in such a way. On the other hand, the Co-TPP complexes coordinated with the other ligands (tetrahydrofuran, quinoline, and some of the pyridine derivatives) took up O_2 weakly and reversibly according to Eq. (2). Inspection of ESR spectra at 10 min after O_2 addition led us to suggest that the degree of O_2 complexing is approximately given by the sequence:

tetrahydrofuran ~ quinoline < 4-cyanopyridine
< 4-methylpyridine < triphenylphosphine
~ pyridine < piperidine < 4-aminopyridine
< benzimidazole < imidazole.

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KEN'ICHI YAMAMOTO
TAKAO KWAN

Faculty of Pharmaceutical Sciences,
The University of Tokyo,
Bunkyo-ku, Tokyo, Japan
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Crystalline Structures of USb_3O_{10} and $USbO_5$ in Acrylonitrile Catalysts*

In an earlier publication (*1*) the existence of two new U–Sb-oxide crystalline phases was reported and their importance in the catalytic synthesis of acrylonitrile from propylene, ammonia, and air was illustrated. Additional study of these crystalline compounds leads to the conclusion that Phase I, reported earlier as $(UO_2)Sb_3O_7$, is better described as USb_3O_{10} and Phase II as $USbO_5$, instead of $Sb_3U_3O_{14}$.

Pure Phase I was prepared by dissolving the excess antimony oxide with HCl from a U–Sb-oxide composition having a high antimony content (U/Sb = 1:9.2). Pure Phase II was prepared by thermal decomposition of Phase I at 1090°C. The heavy atom ratio of the compounds was assessed by wet test methods (*2*) and X-ray fluorescence analysis.

The crystal structure of Phase I was determined from powder diffraction data and by analogy to the single crystal work of Chevalier and Gasperin (*3*) on the UNb_3O_{10} and related systems. As shown in Table 1, the USb_3O_{10} compound (in which the d calculations come from our lattice constants and the intensity calculations come from the x,y,z and B's of Chevalier and Gasperin (*3*) for UNb_3O_{10}) has orthorhombic symmetry and belongs to the *Fddd* space group. All of the previously observed lines (*1*) could be assigned, and more importantly the fit between calculated

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TABLE 1
X-RAY DIFFRACTION DATA FOR PHASE I

Formula: USb_3O_{10}; system, orthorhombic.
$a = 7.346$ Å Space group $Fddd - D_{2h}^{24}$
$b = 12.72$ $\rho_{obs} = 7.34$ g/cc, $\rho_{calc} = 7.05$
$c = 15.40$
$Z = 8$

hkl	d_{obs}	d_{calc}	I_{obs}	I_{calc}	
111	5.89	5.88	5	6.6	
022	4.90	4.90	3	5.7	
113[a]	—	3.99	—	7.0	
004	3.85	3.85	67	58.2	
131[b]	—	3.57	—	1.3	
202	—	3.32	—	1.7	
040	3.18	3.18	100	35.8	106.0
220		3.18		70.2	
133	2.98	2.99	4	2.4	
222	—	2.94	—	0.0	
115	—	2.77	—	0.3	
044	2.45	2.45	61	22.4	65.8
224		2.45		43.4	
026	2.37	2.38	4	0.8	4.1
151		2.38		1.7	
311		2.38		1.5	
135		2.36		0.1	
242	2.29	2.30	4	4.0	
153	2.18	2.18	3	4.5	
313		2.18			
—[c]					
008	1.920	1.924	12	10.4	
400	1.834	1.836	29	9.0	26.1
260		1.836		17.1	
404	1.657	1.657	30	9.0	26.2
264		1.657		17.2	
048	1.645	1.647	33	9.1	26.8
228		1.647		17.7	
080	1.589	1.590	14	4.4	13.3
440		1.590		8.9	
084	1.468	1.470	19	4.8	14.5
444		1.470		9.7	
408	1.329	1.330	18	5.0	14.5
268		1.328		9.5	

[a] Under β of 004.

[b] Under β of 040, 220.

[c] Beyond this point, only observed lines are tabulated; all unobserved lines have a calculated intensity of less than 2.0. $R = \Sigma|I_0 - I_c|/\Sigma I_0 = 0.124$

and observed intensities is excellent, including unobserved lines all of which are calculated to be quite weak. The agreement between calculated and observed densities is good. A second calculation was made omitting the oxygen atoms from the structure; the R-factor increased from the 0.124 of Table 1 to 0.259. Thus, the chemical formula, USb_3O_{10}, is substantiated by the first calculation, and the positions of the oxygen atoms are defined clearly enough to give reliable metal atom coordination and reasonably good interatomic distances. These distances are listed for the 8-coordinate U and 6-coordinate Sb in Table 2. They are in agreement with the general trends in U and Sb oxygen compounds (*4*). One interesting result of this structure is a very short $U\text{–}O_{III}$ distance, 1.80 Å, which is in good agreement with a short U–O distance postulated earlier (*1*) based on low frequency infrared results (930 cm^{-1}).

Phase II, $USbO_5$, is structurally very similar to Phase I as shown by comparison of the respective diffraction patterns. Replacement of the Sb in equipoint (b) of *Fddd* in USb_3O_{10} by U leads to $UUSb_2O_{10}$ or $USbO_5$, with now 16 formula weight per unit cell. Indexing of the powder pattern leads to the results in Table 3. A similar replacement of Nb by Ti has also been observed by Chevalier and Gasperin (*5*).

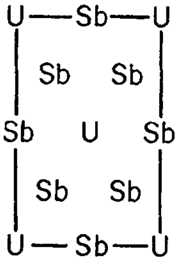
A calculation of intensities in *Fddd*, with the replacement of Sb by U, for $USbO_5$ was made in the same way as for USb_3O_{10}. All of the major lines ($I/I_1 > 5$) fitted quite well, both in d-spacing and intensity; however, some of the weaker lines did not have their intensities satisfactorily accounted for, as did all of the lines fitted in the calculation for Phase I. With the oxygens included and with the Miller indices of all of the strong lines and most of the weak lines made as for Phase I, an R-factor of 0.239 resulted. Without the oxygen $R =$ 0.341. An attempt was made to fit the data for Phase II to the structure of UVO_5 in space group *Pbcm* (*6*). In the latter case, the agreement was much worse than for the *Fddd* structure. Other postulated orthorhombic arrangements of the heavy U and Sb atoms were investigated, but none gave as good agreement as the *Fddd* structure. Hence, it appears that Phase II has the heavy atoms at positions close to those of Phase I, but with a distortion of all atoms leading to a lower symmetry subgroup.

Nevertheless, the two structures are

TABLE 2
INTERATOMIC DISTANCES (Å) FOR PHASE I—USb_3O_{10}

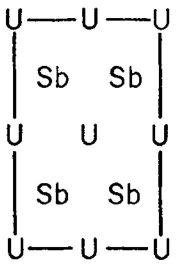
$U–O_I$ (4) = 2.44	$Sb_I–O_I$ (4) = 2.04	$Sb_{II}–O_I$ (2) = 1.93
$U–O_{III}$ (2) = 1.80	$Sb_I–O_{II}$ (2) = 1.85	$Sb_{II}–O_{II}$ (1) = 1.88
$U–O_{IV}$ (2) = 2.54		$Sb_{II}–O_{III}$ (1) = 2.17
		$Sb_{II}–O_{IV}$ (2) = 1.95
$(U–O)_{av}$ = 2.31	$(Sb_I–O)_{av}$ = 1.98	$(Sb_{II}–O)_{av}$ = 1.97

closely related. This can be shown in the following way, considering heavy atoms only:



USb_3O_{10}

(at z = 0.000)
Phase I



$USbO_5$

(at z = 0.000)
Phase II

Actually, the structures are pseudohexagonal, related to α-UO_3, as has been found by Kovba and co-workers (7) in some other mixed uranium oxide systems.

TABLE 3
UNIT CELL FOR PHASE II

Formula $UsbO_5$; system, orthorhombic.

a = 7.53 Å
b = 13.04
c = 15.80
Z = 16
ρ_{obs} = 7.74 g/cc, ρ_{calc} = 7.53

In all cases the superstructure is orthorhombic.

More complete discussion of the above including additional physical data will be reported shortly.

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ROBERT K. GRASSELLI
DEV D. SURESH

The Standard Oil Company (Ohio)
Cleveland, Ohio 44128

KERRO KNOX

Cleveland State University
Cleveland, Ohio 44115

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Controlled Impregnations Via Displacement of an Immiscible Liquid

The initial step in the preparation of a supported catalyst is the impregnation of the support with a solution of the desired metal salt. As ordinarily carried out in the laboratory, impregnations are rather ill-defined. Thus, the repetitive sequence of