physical displacements towards the neighbouring un-occupied octahedral positions. After two F_o–F_c syntheses R for the $hk0$ reflexions was 10·6%. The ambiguities of space group noted for $W_3Nb_{14}O_{44}$ apply equally to the present case for the same reasons. For the 104 observed hkl data, R for $I\bar{4}$ was 16·0% and for $I4/m$ 17·8%. Parameters are listed in Table 5, bond lengths in Table 6, and F_o and F_c in Table 7 where the value for B (isotropic) is 0·3 Å^{-2}.

Discussion

The structures of the tetragonal phases are illustrated by Figs. 3 and 4. In projection, the octahedral metal atoms appearing at both levels form rows exactly parallel and at right angles to each other. These orthogonal groups, constituting the bulk of the scattering matter in both structures, are primarily responsible for the crystallographic sub-cell and contribute little or nothing to the remainder of the reflexions, most of which are below the observable limit. The tetrahedral tungsten atoms, on the other hand, are not collinear and interrupt each row at finite intervals; being in the special positions (0 $\frac{1}{2}$ $\frac{1}{4}$) they contribute equally to all $hk0$ reflexions. Projections of electron density based

upon the observed data, therefore contain only a small fraction of them, and it is not surprising that the octahedral metals appeared as well shaped peaks, while the tetrahedral atoms, for which so much necessary information was missing, did not.

It is difficult to discuss variations of interatomic distance with any assurance as the standard deviations are so large. The tetrahedral dimensions are almost the same for both compounds, $1·76 \pm 0·12$ Å for the W–O distances and 106·0° and 113·3° for the O–W–O angles in $W_3Nb_{14}O_{44}$, and $1·77 \pm 0·14$ Å together with 106·7° and 115·3° for $W_8Nb_{18}O_{69}$. These can be compared with the W–O distances of $1·70 \pm 0·07$ Å for $WNb_{12}O_{33}$ and 1·76 and $1·85 \pm 0·07$ Å for $W_5Nb_{16}O_{55}$. The octahedra at the centres of the blocks, $B(1)$ for $W_3Nb_{14}O_{44}$ and $B(2)$ and $B(3)$ for $W_8Nb_{18}O_{69}$ appear to be no more regular than the others (Tables 4 and 6), but this may simply be a consequence of the large uncertainties. In all other respects the dimensions appear to be normal.

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Multiple Phase Formation in the Binary System Nb_2O_5–WO_3.
IV. The Block Principle

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The four new phases found in the Nb_2O_5–WO_3 system each contain octahedral blocks of a specific size, joined in a manner which leaves tetrahedral positions for some of the metal atoms. The many ways in which logical structures containing blocks of octahedra can be devised are briefly discussed. These can all be summarized by a general formula containing several independent variables, representing the size of block and its mode of packing.

The niobium-tungsten mixed oxide phases

At the outset of this study (Roth & Wadsley, 1965b) an attempt was made to predict the compositions of previously unsuspected mixed-oxide phases of niobium and tungsten. These predictions were based upon certain relationships between a number of other niobates, from which it was supposed that structurally related homologues might exist in the Nb_2O_5–WO_3 compos-

ition region. Although one and possibly two of these new phases were found, namely $WNb_{12}O_{33}$ and $WNb_{30}O_{78}$, there were three which did not fit exactly into this preconceived pattern. Their structures were nevertheless related in a logical way, and they are now discussed in this paper.

Each metal atom in the cubic ReO_3-type structure is in octahedral coordination with oxygen, and every oxygen atom is common to two metals. The three-dimensional structure, therefore, contains octahedra all sharing corners, and is conveniently pictured as a chessboard pattern of squares each representing an

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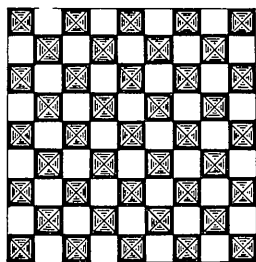* Permanent address: National Bureau of Standards, Washington D.C., U.SA.

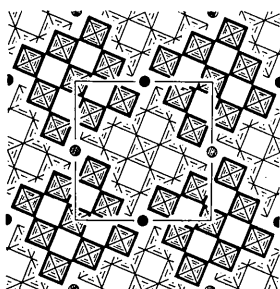Fig. 1. The ReO₃-type structure in projection. Each square represents an octahedron.

Fig. 2. Idealized structure of PNb₉O₂₅ containing blocks 3 octahedra wide, 3 long, and infinite out of plane of the paper. Circles are tetrahedral P.

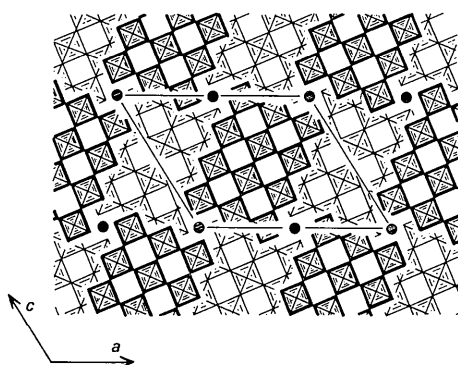Fig. 3. Idealized structure of WNb₁₂O₃₃, the blocks being 3 × 4 × ∞, and tungsten in the tetrahedral positions (circles).
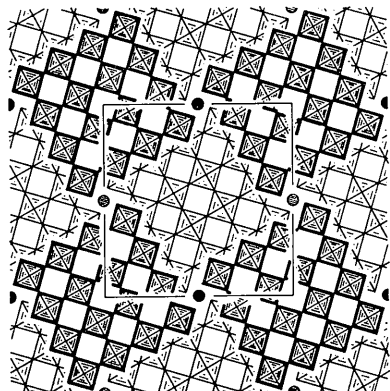
Fig. 4. Idealized structure of W₃Nb₁₄O₄₄, the blocks 4 × 4 × ∞.

octahedron seen in projection down a body diagonal (Fig. 1). Despite its simplicity this arrangement is found in very few oxides, although it is adopted by the oxy-fluorides NbO₂F and TiOF₂ as well as certain closely related trivalent metal fluorides, some of which may have rhombohedral instead of cubic symmetry. But it does occur in modified form as the blocks of finite size in all of the high-temperature niobium oxides containing Ti, P and W as substituent elements.

The structures of the four tungsten-niobium oxides, determined in the two previous papers (Roth & Wadsley, 1965c, d), are summarized in Table 1 and illustrated in idealized form by Figs. 3–6. They are all directly related to PNb₉O₂₅, shown in Fig. 2 (Roth, Wadsley & Andersson, 1965). Each one contains ReO₃-type octahedral blocks of the same size, joined to similar blocks at different levels along the short axis by edge-sharing, and there are two tetrahedral positions at the junctions of every four blocks. Starting with WNb₁₂O₃₃ the block size was found to be 3 octahedra by 4 as predicted. But W₃Nb₁₄O₄₄ had blocks 4 × 4, W₅Nb₁₆O₅₅ 4 × 5, while in W₈Nb₁₈O₆₉ they were 5 × 5. In all cases the blocks were infinite out of the
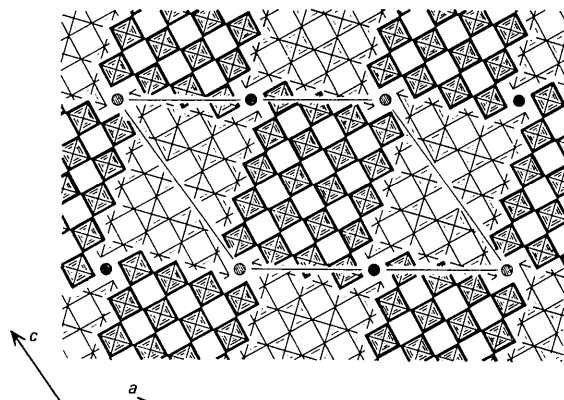
Fig. 5. Idealized structure of W₅Nb₁₆O₅₅, the blocks 4 × 5 × ∞.
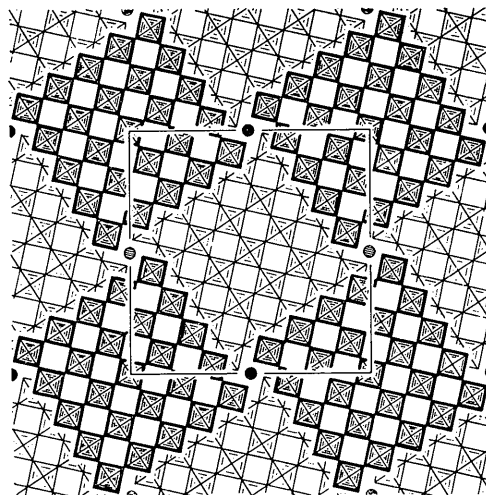
Fig. 6. Idealized structure of W₈Nb₁₈O₆₉, the blocks 5 × 5 × ∞. The terminal member of the Nb/W oxides with the formula $B_{nm+1}O_{3nm-(n+m)+4}$.

plane of the paper. Where there were the same number of octahedra in length and breadth the symmetry of the phase was tetragonal, and when the blocks in projection were rectangular it was monoclinic. For all compounds except $WNb_{12}O_{33}$, the Nb and some of the W atoms statistically occupied the octahedral positions, and disorder was not present in the blocks themselves, as might have been the case if the phases were at all ill-defined or showed extensive regions of homogeneity. The Nb atoms in $WNb_{12}O_{33}$ were octahedral.

In all compounds the tetrahedra were aligned parallel to the monoclinic b or the tetragonal c axes forming continuous linear strings of interstitial positions, half of which contained tungsten atoms. These are characteristics of tunnel structures, where the ordered sequence of filled and empty sites in any one tunnel may have no relation to the corresponding sequences in adjacent tunnels (Wadsley, 1964). In the structure analyses of all four phases we attempted to distinguish complete order from this restricted kind of disorder requiring changes of space group, but without reaching any satisfactory general conclusions.

The greater the block size, the more difficult the compounds were to prepare as single phases. $W_5Nb_{16}O_{55}$ began to disproportionate on annealing at 1000 °C, while $W_8Nb_{18}O_{69}$ could only be prepared by quenching from 1350 °C. We were unable to make any of the compounds listed under the sub-heading in Table 1, where the blocks would be 5×6, 6×6, 6×7 etc. The series therefore terminated with $W_8Nb_{18}O_{69}$, and the next four phases richer in WO_3 which were formed at 1350 °C (Roth & Wadsley, 1965b) are doubtless the members of a new series of structurally related stoichiometric compounds, but with a building principle of a different kind.

Ranges of homogeneity

With the possible exception of $WNb_{12}O_{33}$ no phase had a detectable range of composition. There appear to be

good reasons for this, if arguments are based upon the most likely models. Vacancies in the oxygen positions upset the coordination of the adjacent metal ions, and it is considered unlikely that they will exist, except perhaps at high temperatures. Stoichiometric variability could also arise if positions within a structure which are normally empty were fractionally occupied by additional metals. There are two such positions. The first are the twelvefold sites which change the ReO_3-type blocks into perovskite-type blocks if they are occupied. These holes are available only to ions with radii in between 0·95 and 1·35 Å (Roth, 1957), but the only metals in the compounds, apart from impurities, are too small to be considered. The second kind are the empty tetrahedra in the tunnels. Additional Nb or W in these would bring two ions to within 1·9 Å (i.e. b/2) of each other, an unlikely event unless either the oxygen atom forming the tetrahedra were moved away from their special planes perpendicular to [010], or the metal ions were displaced towards the four empty octahedral positions adjacent to each tetrahedron (Gatehouse & Wadsley, 1964). This was considered for the tetragonal phases and rejected on other grounds.

Possible structures containing ReO_3–type blocks

The present study originated with the idea that phases prepared by reacting Nb_2O_5 and WO_3 in the solid state might be homologues of several previously reported high temperature niobium oxides. These had been classified into four structurally related groups (Roth & Wadsley, 1965b), each one with blocks of octahedra three wide, and three, four or five long, packed in certain characteristic ways. The new phases were expected to retain the general features of some or all of the four groups, but containing longer ReO_3-type blocks, still three octahedra wide, and related therefore to a 'parent' phase B_3O_8 having the structure recently reported for Nb_3O_7F (Andersson, 1964b), where the block size was $3 \times \infty \times \infty$. Although this did not eventuate, we

Table 1. *Ternary oxides of niobium containing single blocks all of one kind*

Known compounds

Mol ratio Nb_2O_5:WO_3	Composition	Size of block (infinite in 3rd dimension)	Symmetry*
	PNb_9O_{25}	3×3	T
6:1	$WNb_{12}O_{33}$	3×4	M
7:3	$W_3Nb_{14}O_{44}$	4×4	T
8:5	$W_5Nb_{16}O_{55}$	4×5	M
9:8	$W_8Nb_{18}O_{69}$	5×5	T

Compounds sought but not found (Roth & Wadsley, 1965b, Table 2)

10:11	$W_{11}Nb_{20}O_{83}$	5×6	M
11:15	$W_{15}Nb_{22}O_{100}$	6×6	T
12:19	$W_{19}Nb_{24}O_{117}$	6×7	M
13:24	$W_{24}Nb_{26}O_{137}$	7×7	T
14:29	$W_{29}Nb_{28}O_{157}$	7×8	M
15:35 (=3:7)	$W_{35}Nb_{30}O_{180}$	8×8	T

* T, Body-centred tetragonal; M, side-centred monoclinic.

can now forsee a number of additional compounds, which might be induced to form under the proper experimental conditions, with structures resembling the members of the four groups but containing the wider blocks $4 \times n \times \infty$ or $5 \times n \times \infty$ instead. They will then be related to new 'parent' phases B_4O_{11} and B_5O_{14}, where the blocks are four and five octahedra in width, instead of to B_3O_8.

In discussing $TiNb_{24}O_{62}$ (Roth & Wadsley, 1965a) where $3 \times 4 \times \infty$ blocks form pairs by edge-sharing at the same level, it was shown that related structures might be derived from it in two ways. Firstly the blocks could be joined in pairs by an alternative method to give a dimorph; secondly, the blocks of the one size could perhaps form larger groups of three, four, etc., by edge-sharing at the same level. The same arguments hold equally well for the wider blocks. Cases could also arise where more than one size of the block was present in a particular structure, and although high-temperature Nb_2O_5 is the only example known up to the present, there are numerous alternative ways of packing two different block sizes together to form a three-dimensional structure of the kind under discussion.

There can be little doubt that the number of these structures that can be devised is very large indeed, and it is equally certain that all of the mixed oxides of Nb and W have not yet been discovered or characterized. Our phase study (Roth & Wadsley, 1965b) was virtually confined to the 1350–1400 °C region, and more compounds with some of these proposed structures could form at other temperatures. Alternatively they might either appear in a closely related ternary system such as TiO_2–Nb_2O_5–WO_3, or be stabilized by a small amount of some other ion.

Representation of the niobium oxides by homologous series formulae

To include the Nb/W oxides, the four groups of compounds A to D each represented by a series formula with a single variable (Roth & Wadsley, 1965b) must be increased to six. The scheme now consists of:

Group A. $B_{3n}O_{8n-3}$. $TiNb_2O_7$ ($n=3$), $Ti_2Nb_{10}O_{29}$ ($n=4$).

Group B. $B_{3n+1}O_{8n-2}$, n odd. Nb_2O_5 ($n=9$), possibly $Nb_{22}O_{54}$ ($n=7$).

Group C. $B_{3n+1}O_{8n-2}$, n even. $TiNb_{24}O_{62}$ ($n=8$), possibly $WNb_{30}O_{78}$ ($n=10$).

Group D. $B_{3n+1}O_{8n+1}$. PNb_9O_{25} ($n=3$), $WNb_{12}O_{33}$ ($n=4$).

Group E. $B_{4n+1}O_{11n}$. $WNb_{12}O_{33}$ ($n=3$), $W_3Nb_{14}O_{44}$ ($n=4$), $W_5Nb_{16}O_{55}$ ($n=5$).

Group F. $B_{5n+1}O_{14n-1}$. $W_5Nb_{16}O_{55}$ ($n=4$), $W_8Nb_{18}O_{69}$ ($n=5$).

The formulae in groups D, E and F, corresponding to the compounds in Figs. 2–6, can be generated by a single expression containing *two* variables n and m, the width and length of a single block,

$$B_{nm+1}O_{3nm-(n+m)+4} .$$

For example if the block is 4 octahedra wide and 5 long, the formula reduces to $B_{21}O_{55}$ and the corresponding compound is $W_5Nb_{16}O_{55}$. To include the members of groups A and C we must introduce a third unknown p, the number of blocks n wide and m long that are joined at the same level by common edges. A new formula

$$B_{nmp+1}O_{3nmp-(n+m)p+4}$$

now summarizes groups A to F with the exception of B, and includes all of the hypothetical structures discussed in the earlier parts of this series containing one size of block, no matter how they are joined. The formula of $TiNb_{24}O_{62}$ is derived as follows: the blocks are 3×4 and are joined in pairs, *i.e.* $n=3$, $m=4$, $p=2$, and the general expression reduces to $B_{25}O_{62}$. A hypothetical compound with blocks 4×5 joined in groups of 3 would be $B_{61}O_{157}$ with the composition $9WO_3$: $26Nb_2O_5$. If this formed a single phase by some appropriate heat treatment, its ideal structure would therefore almost certainly be known.

This formula with three variables can be expressed as a three-dimensional table of compounds, part of which is set out in Table 2 in two-dimensional sections of the kind devised independently by Andersson (1964a). Each section is represented by a single homologous series formula containing two variables, and each row of a section, horizontal as well as vertical, by a formula with only one. Every section is symmetrical about a diagonal, and the relationship of any member of the table to a parent oxide, BO_3, with the ReO_3-structure can be worked out. The first section, $p=1$, contains the compounds with single blocks, groups D, E, and F. Only two compounds that are known appear in the second section, $p=2$, where the blocks are joined in pairs, group C. The third section, $p=\infty$, contains the two titanoniobates of group A where the blocks are joined endlessly through structures with no characteristic tetrahedral positions at the junctions. One or two additional compounds are included to illustrate the generality of the table, but most are hypothetical phases.

The formula represents only those compounds where the blocks, which are centred around two levels perpendicular to the short axes of symmetry, are all of the one size. Where there are *two* sizes of block, as in group B, a general equation to represent all of the possibilities must contain six unknowns, not three. Structural formulae for group B can nevertheless be derived by using the above formula twice, that is to say once for each level and adding the results together. Thus for Nb_2O_5, $n=3$, $m=5$, $p=\infty$ for one level, while $n=3$, $m=4$, $p=1$ at the other: the formula becomes $B_{15}O_{37} + B_{13}O_{33} = B_{28}O_{70}$.

In the present case it is questionable whether this formalism of the homologous series has any practical use. The general formula in three unknowns gives the com-

position for a given type of structure but can only be used backwards. It can have only slight chances of success if used to derive the possible structures occurring at a given composition. Not only will there be several likely alternatives, but there is always the possibility either of additional cases such as those of group B where the formula must be used twice, or of different building schemes we have neither found nor foreseen. As more compounds are added to this particular system, their representation as an homologous series will probably become more complicated by the addition of new variables.

Conclusions

The inevitable questions raised by this study are 'Why does the series of Nb/W oxides stop at the phase $W_8Nb_{18}O_{69}$, and why do they adopt this particular principle rather than some other one which is equally likely?' An analysis of bond lengths, summarized in Table 3 for all the compounds examined in these laboratories, shows no significant trends towards some stereochemical limits, and so answers must eventually be sought elsewhere.

A compound forming at a particular composition and temperature must necessarily have a minimum free energy of formation. It can be assumed that the heats of formation of these compounds per mole of constituent oxide do not vary appreciably, and any variations in free energy are due primarily to differences in entropy. The problem is then one of entropy of ordering, which reaches some minimum value for each compound only when the blocks are as symmetrical as possible – otherwise there is no obvious reason why the wider blocks should exist at all. The factor limiting the number of phases must then lie with the blocks themselves; when they have reached a certain size the long-range order parameters become ineffective, and thermodynamically stable phases with the same building principles no longer exist.

Table 2. *Generation of structural formulae by the series* $B_{nmp+1}O_{3nmp-(n+m)p+4}$

Section $p=1$

$m \rightarrow$ $\downarrow n$	1	2	3	4	5	m	∞
1	B_2O_5	B_3O_7	B_4O_9	B_5O_{11}	B_6O_{13}	$B_{m+1}O_{2m+3}$	BO_2
2	B_3O_7	B_5O_{12}	B_7O_{17}	B_9O_{22}	$B_{11}O_{27}$	$B_{2m+1}O_{5m+2}$	B_2O_5 (V_2O_5)
3	B_4O_9	B_7O_{17}	$B_{10}O_{25}$ (PNb_9O_{25})	$B_{13}O_{33}$ ($WNb_{12}O_{33}$)	$B_{16}O_{41}$	$B_{3m+1}O_{8m+1}$	B_3O_8 (Nb_3O_7F)
4	B_5O_{11}	B_9O_{22}	$B_{13}O_{33}$ ($WNb_{12}O_{33}$)	$B_{17}O_{44}$ ($W_3Nb_{14}O_{44}$)	$B_{21}O_{55}$ ($W_5Nb_{16}O_{55}$)	$B_{4m+1}O_{11m}$	B_4O_{11}
5	B_6O_{13}	$B_{11}O_{27}$	$B_{16}O_{41}$	$B_{21}O_{55}$ ($W_5Nb_{16}O_{55}$)	$B_{26}O_{69}$ ($W_8Nb_{18}O_{69}$)	$B_{5m+1}O_{14m-1}$	B_5O_{14}
n	$B_{n+1}O_{2n+3}$	$B_{2n+1}O_{5n+2}$	$B_{3n+1}O_{8n+1}$	$B_{4n+1}O_{11n}$	$B_{5n+1}O_{14n-1}$	$B_{nm+1}O_{3nm-(n+m)+4}$	B_nO_{3n-1}
∞	BO_2	B_2O_5 (V_2O_5)	B_3O_8 (Nb_3O_7F)	B_4O_{11}	B_5O_{14}	B_nO_{3n-1}	BO_3 (ReO_3)

Section $p=2$

$m \rightarrow$ $\downarrow n$	1	2	3	4	5	m	∞
1	B_3O_6	B_5O_{10}	B_7O_{14}	B_9O_{18}	$B_{11}O_{22}$	$B_{2m+1}O_{4m+2}$	B_2O_4
2	B_5O_{10}	B_9O_{20}	$B_{13}O_{30}$	$B_{17}O_{40}$	$B_{21}O_{50}$	$B_{4m+1}O_{10m}$	B_4O_{10} (V_2O_5)
3	B_7O_{14}	$B_{13}O_{30}$	$B_{19}O_{46}$	$B_{25}O_{62}$ ($TiNb_{24}O_{62}$)	$B_{31}O_{78}$ ($WNb_{30}O_{78}$)	$B_{6m+1}O_{16m-2}$	B_6O_{16} (Nb_3O_7F)
4	B_9O_{18}	$B_{17}O_{40}$	$B_{25}O_{62}$ ($TiNb_{24}O_{62}$)	$B_{33}O_{84}$	$B_{41}O_{106}$	$B_{8m+1}O_{22m-4}$	B_8O_{22}
5	$B_{11}O_{22}$	$B_{21}O_{50}$	$B_{31}O_{78}$ ($WNb_{30}O_{78}$)	$B_{41}O_{106}$	$B_{51}O_{134}$	$B_{10m+1}O_{28m-6}$	$B_{10}O_{28}$
n	$B_{2n+1}O_{4n+2}$	$B_{4n+1}O_{10n}$	$B_{6n+1}O_{16n-2}$	$B_{8n+1}O_{22n-4}$	$B_{10n+1}O_{28n-6}$	$B_{2nm+1}O_{6nm-2(n+m)+4}$	$B_{2n}O_{6n-2}$
∞	B_2O_4	B_4O_{10} (V_2O_5)	B_6O_{16} (Nb_3O_7F)	B_8O_{22}	$B_{10}O_{28}$	$B_{2n}O_{6n-2}$	B_2O_6 (ReO_3)

Section $p=\infty$

$m \rightarrow$ $\downarrow n$	1	2	3	4	5	m	∞
1	BO	B_2O_3	B_3O_5	B_4O_7	B_5O_9	B_mO_{2m-1}	BO_2
2	B_2O_3	B_4O_8 ($AlNbO_4$)	B_6O_{13} (V_6O_{13})	B_8O_{18}	$B_{10}O_{23}$	$B_{2m}O_{5m-2}$	B_2O_5 (V_2O_5)
3	B_3O_5	B_6O_{13} (V_6O_{13})	B_9O_{21} ($TiNb_2O_7$)	$B_{12}O_{29}$ ($Ti_2Nb_{10}O_{29}$)	$B_{15}O_{37}$	$B_{3m}O_{8m-3}$	B_3O_8 (Nb_3O_7F)
4	B_4O_7	B_8O_{18}	$B_{12}O_{29}$ ($Ti_2Nb_{10}O_{29}$)	$B_{16}O_{40}$	$B_{20}O_{51}$	$B_{4m}O_{11m-4}$	B_4O_{11}
5	B_5O_9	$B_{10}O_{23}$	$B_{15}O_{37}$	$B_{20}O_{51}$	$B_{25}O_{65}$	$B_{5m}O_{14m-5}$	B_5O_{14}
n	B_nO_{2n-1}	$B_{2n}O_{5n-2}$	$B_{3n}O_{8n-3}$	$B_{4n}O_{11n-4}$	$B_{5n}O_{14n-5}$	$B_{nm}O_{3nm-(n+m)}$	B_nO_{3n-1}
∞	BO_2	B_2O_5 (V_2O_5)	B_3O_8	B_4O_{11}	B_5O_{14}	B_mO_{3m-1}	BO_3 (ReO_3)

Table 3. *Summary of interatomic distances* (Å)

| Compound | Octahedral Metal–oxygen | | | Oxygen–oxygen | | | Tetrahedral |
	Average	Maximum	Minimum	Average	Maximum	Minimum	Average
PNb_9O_{25}	1·98	2·30	1·76	2·79	3·05	2·57	1·65
$WNb_{12}O_{33}$	1·99	2·18	1·80	2·79	3·41	2·15	1·70
$W_3Nb_{14}O_{44}$	1·99	2·18	1·78	2·78	3·19	2·38	1·76
$W_5Nb_{16}O_{55}$	1·97	2·17	1·81	2·78	3·36	2·22	1·76
$W_8Nb_{18}O_{69}$	1·98	2·24	1·74	2·78	3·03	2·50	1·77
Nb_2O_5	1·99	2·26	1·73	2·80	3·25	2·28	1·67
$TiNb_{24}O_{62}$	2·01	2·41	1·72	2·80	3·23	2·31	1·67
$Ti_2Nb_{10}O_{29}$	1·99	2·47	1·72	2·78	3·25	2·37	—
$TiNb_2O_7$	1·99	2·34	1·64	2·77	3·20	2·36	—

Whether a composition corresponds to a discrete phase depends upon whether there is a logical way for blocks of specific sizes to pack together, but it is still a matter for experiment to find out the conditions under which it is formed. Any phase must contain an integral number of metal and oxygen atoms in the unit cell, but its formula need not necessarily be simple, and will almost certainly not be variable to any marked degree. In general the concepts of non-stoichiometric phases in equilibrium systems are all too often deceptive, and have tended to obscure a wealth of subtle detail, now recognizable as multiple phase formation based in the present instance upon building block principles.

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The Structure
of 1-(4-Chlorobenzyl)-1-nitroso-2-(4,5-dihydro-2-imidazolyl)hydrazine Monohydrate

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The monohydrate of 1-(4-chlorobenzyl)-1-nitroso-2-(4,5-dihydro-2-imidazolyl)hydrazine crystallizes from water as clear, colorless, acicular crystals. The cell dimensions are:

$$a_0 = 10·434 \pm 0·004, \quad b_0 = 11·352 \pm 0·004, \quad c_0 = 11·245 \pm 0·004 \text{ Å}; \quad \beta = 108·34° .$$

The space group is $P2_1/c$ with four molecules per unit cell. The intensities of 1885 reflections with $2\theta \le 100·0°$ (copper radiation) were measured with a proportional counter. The 1593 reflections which were 1·1 times the background were considered observed and used in the analysis. The structure was refined by least squares to a final residual R of 9·6 % for all the observed reflections.

The molecule is a normal *N*-nitroso compound with no unusually short intramolecular distances involving the heavy atoms. The N–O distance of 1·250 Å is comparable to the N–O distance found in similar nitroso compounds. The molecules are joined by five types of hydrogen bond: N–H · · · N, N–H · · · O, O–H · · · O, O–H · · · N and C–H · · · O. The existence of the C–H · · · O hydrogen bond is rather unusual but appears to be real.

Introduction

Certain *N*-nitroso compounds can be cyclized to tetrazoles, sydnones, or oxatriazoles by elimination of a molecule of water or ammonia. Benson (1947) reported that compounds of the type R–N(NO)–NH–C(R')=NH, where R' is cyano or 2,4-dibromophenyl, yield substituted tetrazoles by elimination of a water molecule. Boyer & Canter (1955) prepared alkyl ψ-oxatriazoles by deamination of R–N(NO)–NH–C(NH₂)=O.