The Structure of $SbNbO_4$, α-Sb_2O_4, and $SbTaO_4$

By A. C. SKAPSKI* and D. ROGERS†

*[*Institute of Inorganic Chemistry, University of Stockholm, Stockholm, Sweden (Present address: Department of Chemistry, Imperial College, London, S.W.7)*]

†(*Department of Chemistry, Imperial College, London, S.W.7*)

$SbNbO_4$, α-Sb_2O_4, and $SbTaO_4$ are isostructural compounds of orthorhombic symmetry. The structure of $SbTaO_4$ was determined in 1938 by Dihlström[1] from a naturally occurring crystal of stibiotantalite, but the positions of oxygen atoms were derived from spatial considerations only. The uncertainty about the correctness of their positions,[2] and the recent determination of the structure of β-Sb_2O_4,[3] have prompted us to start an accurate re-investigation.

Small, colourless prisms of $SbNbO_4$ were obtained by heating a mixture of antimony trioxide and niobium pentoxide in an evacuated quartz capsule, using an excess of antimony trioxide as a flux. The unit-cell dimensions are $a = 5{\cdot}561 \pm 0{\cdot}003$, $b = 4{\cdot}939 \pm 0{\cdot}002$, $c = 11{\cdot}810 \pm 0{\cdot}003$ Å, $U = 324{\cdot}4 \pm 0{\cdot}4$ Å^3, in quite good agreement with those obtained by Keller.[4] $D_{obs} = 5{\cdot}68$ g.cm.$^{-3}$, $D_{calc} = 5{\cdot}70_5$ g.cm.$^{-3}$ for a cell content of $4(SbNbO_4)$. The space group has proved to be $Pna2_1$.

The structure has been determined from 508 independent reflections measured with a goniostat, using Mo-$K\alpha$ radiation. Least-squares refinement has now reached $R = 0{\cdot}045$, and is being continued.

The position of the "heavy" atoms determined by Dihlström have proved to be very nearly correct, but it was found necessary to replace the entire oxygen structure by its approximate mirror image in the plane $z = \frac{1}{4}$. The structure found has many features in common with that of β-Sb_2O_4.

Thus it consists of corrugated sheets of Nb–O octahedra, linked by sharing corners, running

[1] K. Dihlström, *Z. anorg. Chem.*, 1938, **239**, 57.
[2] A. F. Wells, "Structural Inorganic Chemistry", 3rd edition, Clarendon Press, Oxford, 1962, p. 678.
[3] D. Rogers and A. C. Skapski, *Proc. Chem. Soc.*, 1964, 400.
[4] C. Keller, *Z. anorg. Chem.*, 1962, **318**, 89.

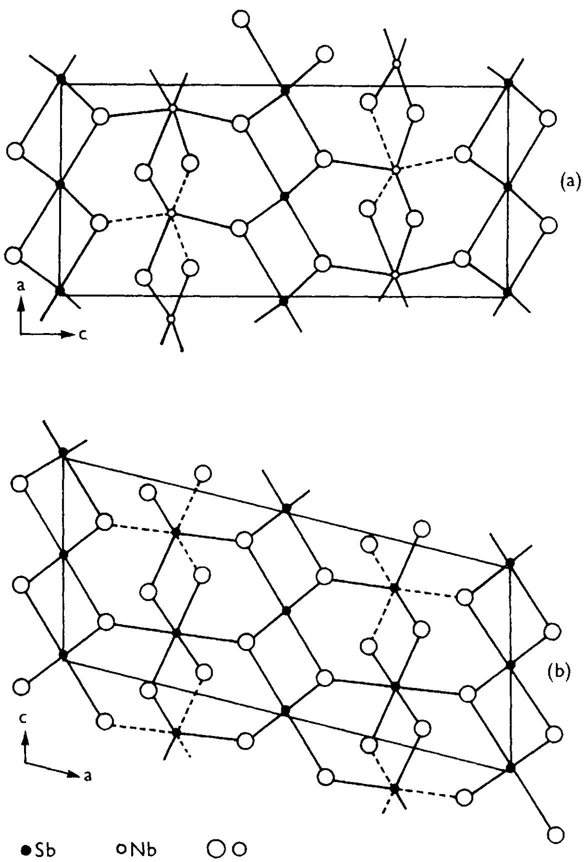

FIGURE 1 (a) [010] *Projection of* $SbNbO_4$.
(b) [010] *Projection of* β-Sb_2O_4 *(origin moved to facilitate comparison)*.

(Dashed lines indicate bonds between niobium and oxygens in the cell below. The octahedra are joined at corners, not edges.)

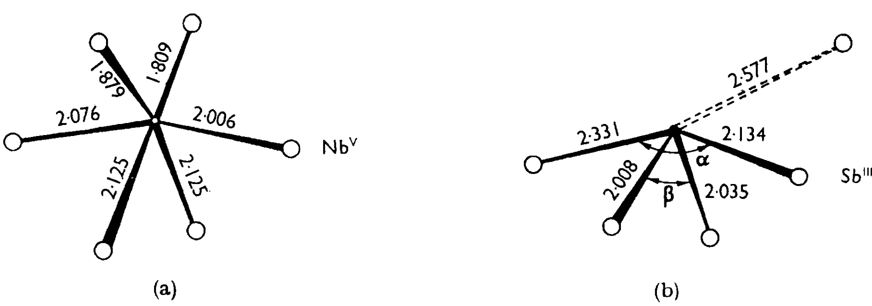

FIGURE 2 (a) Nb^{V} *Co-ordination.*
(b) Sb^{III} *Co-ordination.* $\alpha = 150{\cdot}7°$; $\beta = 92{\cdot}1°$.

(Standard deviation of bonds is $\sim$0·009Å, *and of angles is* $\sim$0·4°.)

parallel to (001). Adjacent sheets in both $SbNbO_4$ and β-Sb_2O_4 are joined by Sb^{III} atoms. If a sheet of octahedra and an adjacent set of Sb^{III} atoms ($Sb^{III}M^{V}O_4$) is symbolized by $\uparrow$, the essential difference between the two structures is the *n* glide perpendicular to *a* in $SbNbO_4$, and can be visualized by writing them as $\uparrow\downarrow\uparrow\downarrow\ldots$ ($SbNbO_4$) and $\uparrow\uparrow\uparrow\uparrow\ldots$ (β-Sb_2O_4). This is shown in Figure 1, and indicates why one is orthorhombic and the other monoclinic. The other two pairs of corresponding projections are rather similar (see Figure 1 in Ref. 3). The co-ordination about Nb^{V} is considerably distorted (see Figure 2a). In α-Sb_2O_4 and $SbTaO_4$, however, where Nb^{V} is replaced by Sb^{V} and Ta^{V} respectively, the metal-to-oxygen bond lengths may differ somewhat from those quoted here. (It is worth noting that the low-temperature, orthorhombic forms of $BiNbO_4$[5] and $BiTaO_4$[6] are also apparently isostructural with stibiotantalite.) The co-ordination about Sb^{III} is one-sided, the four short bonds lying as in β-Sb_2O_4 (see Figure 2b). Four more oxygen atoms lie farther off on the other side: one approaches to a distance of 2·577 Å (the other distances are 3·048, 3·386 and 3·527 Å), whereas in β-Sb_2O_4 the corresponding distances are two of 2·949 Å, and two of 3·044 Å.

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[5] R. S. Roth and J. L. Waring, *J. Res. Nat. Bur. Stand.*, 1962, **66A**, 451.
[6] R. S. Roth and J. L. Waring, *Amer. Min.*, 1963, **48**, 1348.