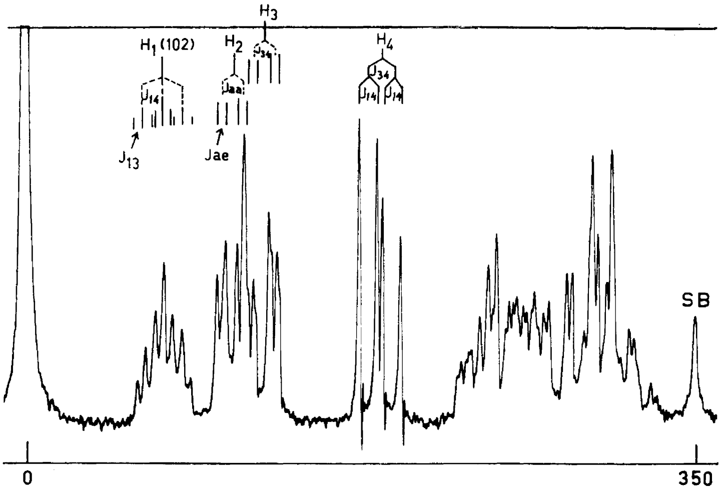

Fig. 2. The NMR-spectrum of 5-hydroxypipecolic acid.

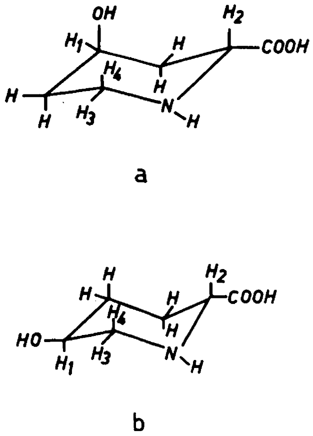

Fig. 3. Molecular conformation of 4-hydroxypipecolic acid (a) and 5-hydroxypipecolic acid (b).

tion of Fig. 3b is consistent with the NMR data for 5-hydroxypipecolic acid.

Witkop and Foltz[5] estimated the configuration of 5-hydroxypipecolic acid, and Clark-Lewis and Mortimer[6] that of 4-hydroxypipecolic acid using a chemical method. Their result is in agreement with ours.

1. Virtanen, A. I. and Kari, S. *Acta Chem. Scand.* **8** (1954) 1290.
2. Virtanen, A. I. and Kari, S. *Ibid.* **9** (1955) 170.
3. Fowden, L. *Biochem. J.* **70** (1958) 629.
4. Virtanen, A. I. and Gmelin, R. *Acta Chem. Scand.* **13** (1959) 1244.
5. Witkop, B. and Foltz, C. M. *J. Am. Chem. Soc.* **79** (1957) 192.
6. Clark-Lewis, J. W. and Mortimer, P. I. *J. Chem. Soc.* **1961** 189.

Received November 9, 1962.

On the Existence of the Suboxides Cr_3O and Mo_3O

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In two papers published in 1954 Schönberg reported the preparation of two new oxides of chromium and molybdenum with the probable formulas Cr_3O [1] and Mo_3O [2]. Neither was obtained as a single phase.

Cr_3O was said to be formed by three different methods, namely (*a*) when Cr_2O_3 was reduced with titanium, vanadium or zirconium at about 1500°C, (*b*) when chromium metal was oxidized by steam in a large excess of hydrogen at 600°C, and (*c*) in trace amounts when chromium metal and Cr_2O_3 were heated in an induction furnace. The oxide was reported to be isomorphous with Cr_3Si ($\beta-W$ structure type) and to have the same cubic cell dimension as this phase.

Mo_3O was obtained by heating mixtures of Mo and MoO_2 at 1000°C and then lowering the temperature to 400°C at a constant rate of 10° per day. A defect version of the *anti*-BiF_3 type structure was proposed for this phase.

No papers confirming the existence of these suboxides have appeared since 1954 and for several reasons a repetition of some of these experiments under more carefully controlled conditions was thought desirable.

Cr_3O. The formation of the phase described as Cr_3O by method (*b*) above was used by Schönberg as evidence that this product was in fact a binary oxide. Thus method (*a*) involved reactions in a ternary system, one component of which was a metal noted for its reactivity towards most crucible materials, while the traces of "Cr_3O" detected in the powder patterns of samples prepared by method (*c*) could easily have been Cr_3Si. For this reason method (*b*) was chosen in the attempts described below to repeat the preparation of Cr_3O.

Hydrogen gas was passed through a tube containing platinized asbestos heated to about 600°C to combine the free oxygen, dried in conc. H_2SO_4 and passed through a tube containing activated carbon at liquid nitrogen temperatures. A given percentage of H_2O was then added by passing the gas through water maintained at 25°C or 0°C after which it was led into a tube of supremax glass and so over an alumina boat containing the chromium to be oxidized. The metal was in the form of a powder crushed to more than 150 mesh. The temperature of the reaction tube was maintained at 600°C during the 24 h period of each experiment. The products were analyzed by means of X-ray powder diffraction patterns recorded in a Guinier focusing camera using Cr$K\alpha$ radiation.

When high grade chromium ("*Ges.f. Elektrometallurgie m.b.H. Werk Nürnberg*", 99.96 % Cr) was used no lines other than those due to Cr and Cr_2O_3 could be observed in the powder patterns of the reaction products, even when long exposure times were used to record the X-ray photographs. Experiments were also made with chromium of the same origin as that used by Schönberg ("*AB Ferrolegeringar*, Stockholm, 99.4 %"). Contamination of this material was demonstrated by the presence in its powder pattern of several additional faint lines. In this case also, however, the only detectable change in the powder patterns after the reaction was the appearance of Cr_2O_3 lines. It is possible that Schönberg attributed some of these impurity lines to "Cr_3O".

The intensity data published for "Cr_3O" [1] are confusing. Since no information is given about the type (or types) of camera used values of I_{calc} cannot be recalculated. On the basis of the proposed structure $p.F^2_{\text{calc}}$-values have been recomputed by the present author, but the ratio between these and the published values of I_{calc} varies in a way which can hardly be accounted for by any probable instrumental ϑ-function (or functions).

Mo_3O. Efforts were made to prepare Mo_3O according to the method given by Schönberg [2]. The starting materials were molybdenum powder ("*Kahlbaum*" or "*Kebo*") and MoO_2 which had been prepared by reducing MoO_3 with hydrogen. These were intimately mixed in the proportions required to give the composition Mo_3O and put into high grade alumina tubes which were sealed inside silica tubes under vacuum. The tubes were heated to 1040°C after which the temperature was reduced to 400°C at a rate of 10° per day by means of a programmed regulator.

The Guinier powder patterns (Cu$K\alpha$ radiation) of the products following this heat treatment did not give even the faintest indication of lines additional to those of the starting materials. The same result was obtained with a sample which had been pressed to a pellet and also with samples heated at 1200°C for one day.

The conclusion that can be drawn from the negative results obtained by these experiments is that the oxides Cr_3O and Mo_3O cannot be reproducibly obtained by the methods reported and at present there seems to be no definite proof of their existence.

Acknowledgements. I wish to thank Professor G. Hägg for suggesting this reinvestigation and Dr. S. Rundqvist for stimulating discussions.

1. Schönberg, N. *Acta Chem. Scand.* **8** (1954) 221.
2. Schönberg, N. *Acta Chem. Scand.* **8** (1954) 617.

Received November 22, 1962.