SHORT COMMUNICATIONS

TWO CRYSTAL FORMS OF TITANIUM(IV) METHOXIDE*

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The structure of metal alkoxides has received considerable attention in recent years[1–7] but polymorphism in this class of compounds has not been reported.

Titanium(IV) methoxide was first prepared by Bischoff and Adkins[8] by an ester interchange reaction. The product (compound A) is a white insoluble powder. Dunn[9] prepared the methoxide from titanium tetrachloride and methanol in the

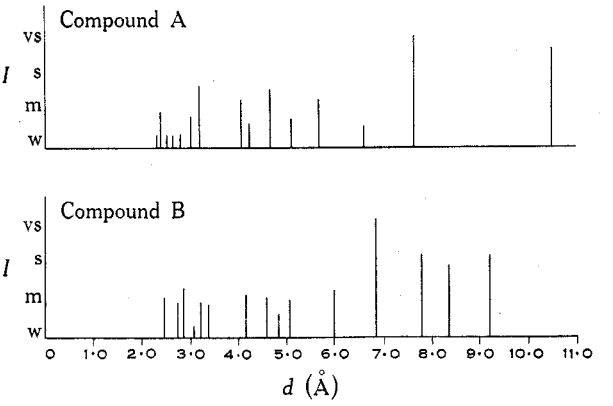

Fig. 1.—Debye–Scherrer diagram.

presence of ammonia. Surprisingly, this material (compound B) is soluble in boiling toluene from which it may be recrystallized. In harmony with the behaviour of the corresponding ethoxide and butoxide[10] in freezing benzene, a concentration dependence of the apparent molecular weight with a limiting association number

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[2] Witters, R. D., and Caughlan, C. N., *Nature*, 1965, **205**, 1312.

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[4] Imam, S. A., *Nature*, 1965, **206**, 1146.

[5] Shearer, H. M. M., and Spencer, G. B., *Chem. Commun.*, 1966, 194.

[6] Wright, D. A., personal communication.

[7] Ibers, J. A., *Nature*, 1963, **197**, 686.

[8] Bischoff, F., and Adkins, H., *J. Am. chem. Soc.*, 1924, **46**, 256.

[9] Dunn, P., *Aust. J. appl. Sci.*, 1959, **10**, 458.

[10] Martin, R. L., and Winter, G., *Nature*, 1963, **197**, 687.

$n = 4$ was observed for compound B. A detailed single crystal X-ray analysis[6] has confirmed its tetrameric nature; its structure is very similar to that of the ethoxide.[7]

The X-ray powder photographs of compounds A and B (see Fig. 1) show strong dissimilarities. Furthermore, there is a significant difference in the far

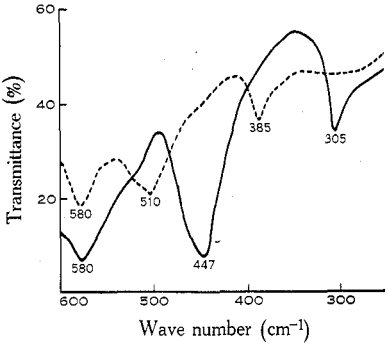

Fig. 2.—Infrared spectra.
——— Compound A;
- - - - compound B.

infrared spectra (600–250 cm^{-1}) of the two compounds in the region where the Ti–(OCH_3) and Ti–(OCH_3)–Ti vibrational modes may be expected[11] (see Fig. 2). It is concluded that two crystal forms are involved.

Experimental

Titanium(IV) *methoxide* was prepared by the two methods described.[8,9] There was no significant difference in the chemical analysis of the two compounds ((A) Found: C, 28·2; H, 6·7; Ti, 27·6. (B) Found C, 26·4; H, 6·6; Ti, 28·0. $Ti(OCH_3)_4$ requires C, 27·9; H, 7·0; Ti, 27·9%).

Infrared spectra (600–250 cm^{-1}) were recorded on a Perkin–Elmer 421 spectrometer using Nujol mulls of the powdered samples between polythene disks.

X-ray powder photographs were taken from powdered samples sealed in quartz capillaries using a Philips camera and nickel-filtered Cu Kα radiation.

[11] Kriegsmann, H., and Licht, K., *Z. Elektrochem.*, 1958, **62**, 1163.