

03.5-13 DISTRIBUTION OF OH IONS IN MIXED OH/F APATITES. By A. Baumer (Lab. de Géologie et Géochimie, Univ. de Nice) and W. E. Klee (Inst. f. Kristallographie, Univ. Karlsruhe)

In connection with fluorine uptake by bone and teeth the distribution of hydroxide and fluoride ions in mixed OH/F apatites has been widely studied, mostly by IR spectroscopy. Quantitative studies have been carried out by F. Freund (Inorg. Nucl. Chem. Letters (1977) 13, 57): As more and more F is introduced into OH apatite the combined intensity of the OH stretching bands increases up to ~ 20 mole-% F and only then shows the expected decrease. No explanation was offered for this interesting phenomenon. We have obtained similar, but not identical results with hydrothermally grown material which may be expected to be more homogeneous than the solid state reaction products of Freund. We have found that the measured intensities can be approximated by the simple function

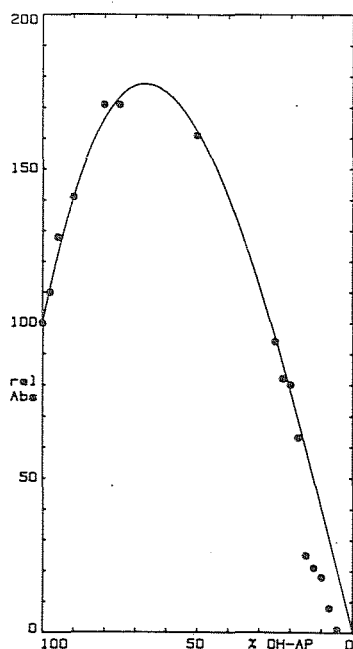
$$I(x) = 100(x^3 + nx(1-x^2)), \text{ where}$$

$I(x)$ is the intensity relative to that of pure hydroxyapatite which is taken as 100

x is the fraction of OH ions
 n is a constant (see below)

The formula can be derived by assuming that
 i) OH and F are distributed statistically
 ii) the absorption of an OH ion in the configuration OH-F is n times the absorption in the configuration OH-OH

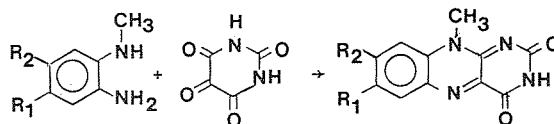
The best fit, obtained for $n=4$, is shown in the Figure.



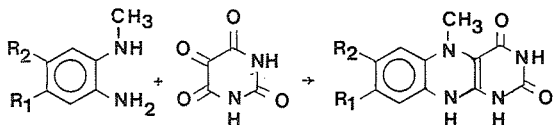
Relative intensities of the OH stretching bands of the mixed apatites $Ca_5(PO_4)_3(OH)_x F_{1-x}$
 Solid circles: measured values
 Curve: calculated values (see text)

03.5-14 IMPORTANCE OF A COMPETING CONDENSATION REACTION IN THE ALLOXAN SYNTHESIS OF FLAVINS. By R.F. Bryan, K.A. Woode, V. Kumar & B.A. Averill, Department of Chemistry, University of Virginia, Charlottesville, VA 22901, U.S.A.

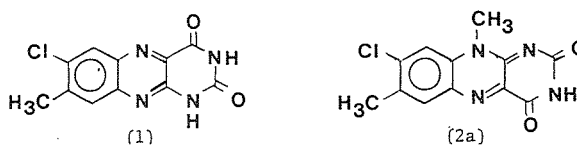
The most widely used synthetic route to the flavins involves the anaerobic condensation of an N-alkyl-o-phenylenediamine with alloxan. It is universally assumed that this condensation proceeds only as shown:



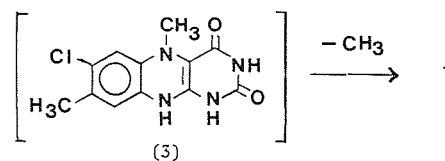
with no important contribution from the alternate path:



Reaction between 5-chloro-4-methyl-N-methyl-o-phenylenediamine [$R_1 = CH_3, R_2 = Cl$], however, yields 7-chloroalloxazine (1) as a significant co-product (30 - 40%) besides the expected 8-chloro-8-nor-flavin (2a).



This implies that the alternate condensation path does play an important role as the 7-chloroalloxazine presumably arises as a result of dealkylation of the thermodynamically unstable intermediate (3). Such N-dealkylations are a familiar feature of flavin chemistry.



Recognition of the importance of the alternate condensation path may explain the great variation in yield for different flavins prepared by this route, and emphasizes the need for caution in the assignment of structure to products of this reaction.

Identification of (1) was by single-crystal X-ray study of its dimethylformamide solvate. $C_{11}H_7ClN_4O_2 \cdot C_3H_7NO$, $a = 8.764(4), b = 16.030(8), c = 11.047(6) \text{ \AA}, \beta = 95.00(2)^\circ, Z = 4, F_2/e, R = 5.6\%$.

Suitable single crystals of (2a) itself could not be prepared. A crystalline derivative (2b) [$R_2 = S(CH_2)_2OH$] was obtained by refluxing (2a) with mercaptoethanol in pyridine under nitrogen. $C_{14}H_{14}N_4O_3S \cdot H_2O$, $a = 9.194(3), b = 9.848(3), c = 11.821(4) \text{ \AA}, \alpha = 87.50(2), \beta = 119.46(3), \gamma = 58.16(2)^\circ, Z = 2, F_1/e, R = 4.7\%$.