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### COPPER (II) COMPLEXES OF VITAMIN D<sub>3</sub> AND 24R,25 DIHYDROXY-VITAMIN D<sub>3</sub>.

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In our investigations on complexing properties of vitamin D<sub>3</sub> and/or its hydroxylated derivatives, we describe here some results obtained with copper (II) and vitamin D<sub>3</sub> and 24R,25-dihydroxy vitamin D<sub>3</sub>.

We have previously demonstrated that CoCl<sub>2</sub> could lead to the following species in aqueous 9 g.L<sup>-1</sup> NaCl (1, 2) : [CoCl<sub>2</sub>(vitD)] (vitD is vitamin D<sub>3</sub>, 25-hydroxyvitamin D<sub>3</sub>, 1 $\alpha$ ,25-dihydroxyvitamin D<sub>3</sub> or 24R,25-dihydroxyvitamin D<sub>3</sub>), [CoCl<sub>2</sub>(vitD)<sub>4</sub>]. The latter complex shows biological effects, depending upon the season (3). The aim of the present work was to determine the chelating properties of vitamin D<sub>3</sub> and 24R,25-dihydroxyvitamin D<sub>3</sub> towards copper (II) in two solvents : methanol (MeOH) and aqueous NaCl.

#### Experimental

As vit. D<sub>3</sub> and its analogues are not very stable in solution, all reagents were always prepared just before their use. The concentrations were, in MeOH 2.10<sup>-4</sup> mol.L<sup>-1</sup> and 2.10<sup>-5</sup> mol.L<sup>-1</sup> in water. The copper solutions (Cu(ClO<sub>4</sub>)<sub>2</sub> in MeOH and CuCl<sub>2</sub> in H<sub>2</sub>O) were prepared in order to obtain the same molarity for the two solutions. The spectra were recorded at 25 °C (298 K) with a Hitachi U 2000 spectrophotometer.

#### Results and discussion

##### Composition of the complexes

The continuous variations curves were drawn using corrected absorbance at a given wavelength  $A_{corr}$  (4, 5) in order to keep only the spectrum of the complex species ( $m$  is related to the metal and  $v$  to the cholecalciferol,  $\epsilon$  is the molar extinction coefficient) :

$$A_{corr} = A_{exp} - (C_m \epsilon_m + C_v \epsilon_v)$$

As the solutions of the cupric ion showed a very weak absorption in the visible region because of their low molarity, it can be assumed that  $\epsilon_m \approx 0$ . The curves were obtained by choosing several wavelengths located around the maximum absorption bands of the vitamin D<sub>3</sub> or its derivatives. The figures 1 and 3 are relative to vitamin D<sub>3</sub> in MeOH and H<sub>2</sub>O respectively whereas figure 2 was obtained with 24R,25-dihydroxyvitamin D<sub>3</sub> in aqueous NaCl.

The curves demonstrate the presence of the complex [Cu(vitD)<sub>4</sub>]<sup>2+</sup> in MeOH and [CuCl<sub>2</sub>(vitD)] and [CuCl<sub>2</sub>(24,25(OH)<sub>2</sub>vitD)] in aqueous NaCl.

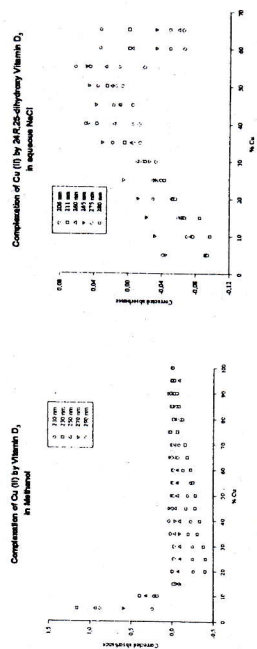


Figure 1

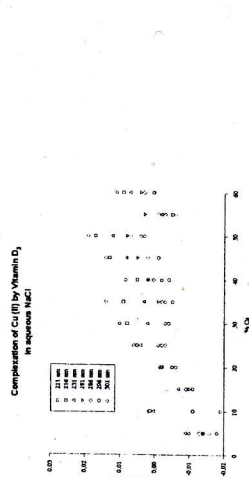


Figure 2

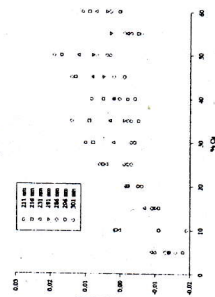


Figure 3

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