References and Notes

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Hollow Crystals from Buffer Solutions of Sodium Diethyl Barbiturate

Abstract. Buffer solutions of sodium 5,5′-diethyl barbiturate, after standing at 4° to 8°C for 7 weeks, were observed to contain large tubular crystals. The crystals appear to have the composition of 5,5′-diethyl barbituric acid. They can be grown readily from fresh seeded solutions.

Large, hollow, tubular crystals in buffer of sodium 5,5′-diethyl barbiturate were unexpectedly observed in this laboratory. Chrysotile asbestos (*1*), halloysite (*1*), pyromorphite (*2*), nitroguanidine (*3*), and vanadinite (*4*) have been previously reported as cavernous, tubular, or hollow crystals. The first two are microscopic; nitroguanidine crystals are about 2 mm long, the vanadinite ones about 10 mm. Various crystal forms of 5,5′-diethyl barbituric acid, of which none were hollow, have been described (*5*). Recently, tubular hexamethylene-tetramine-triphenol was reported (*6*). Because of their unusual form, dimensions, and pyrimidine nature, the observed crystals are described here.

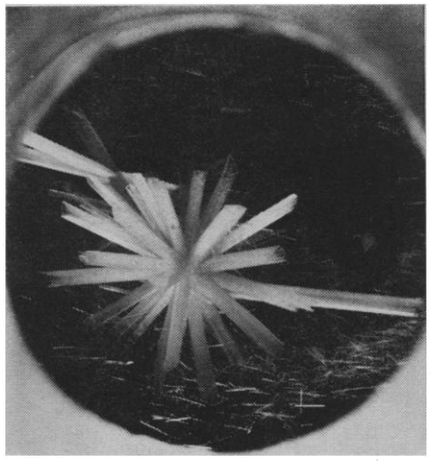

Fig. 1. Appearance of rosette of crystals in mother liquor (about × ½).

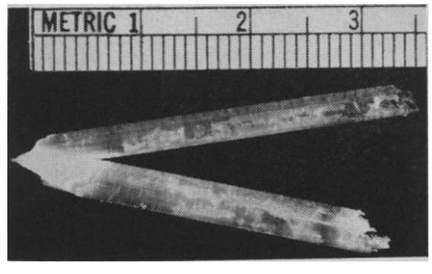

Fig. 2. A pair of tubes, unseparated; removed from rosette. Scale numbers represent centimeters.

16.0 gm of NaOH (reagent grade, Merck) and 88.4 gm of 5,5′-diethyl barbituric acid (N.F. Barbital Merck) were dissolved in water at a total volume of 4 liters. The solution was inadvertently left unstoppered at 4° to 8°C for about 7 weeks. During that period, crystal growth occurred to produce the large rosette shown in Fig. 1. The rosette consists of 30 hollow tubes, each with parallel outer edges in the long axis, all radiating from a common area at a closed end of each tube. Each tube was open at the other end and was about 30 to 40 mm long. The tubes could be broken away in smaller clusters, in pairs (Fig. 2), or as single crystals. Each central end was pointed and solid, not hollow. The two crystals shown in Fig. 2 formed an angle of 17 ± 0.5 deg with each other. The open shaft in one crystal (Fig. 2) was found to end 3 mm from the pointed, closed tip, and in all crystals the open shaft extended to a similar distance from the tip. The tubes were 2 to 4 mm in outside diameter, colorless, moderately translucent, brittle, and smooth to the touch. The outer edges of four crystals, measured in photographs, were found to be parallel (± 0.2 mm over a length of 20 mm).

For analysis, crystals were removed from the rosettes while in the mother liquor by means of a slight wedging motion of a spatula. After the fluid contents from the interior of each had been aspirated with a fine capillary, and the crystals had been washed inside and out quickly with cold water, the separated tubes were dried in a desiccator at 12 mm-Hg over P_2O_5 for 18 hours. After being dried they were sectioned transversely with a razor blade; some fracturing occurred. The open ends could be gently ground until somewhat flat. The interior and contours of the walls were somewhat hexagonal (see Fig. 3).

Analysis showed mp 181° to 184°C (uncorrected) with simultaneously measured mp on acid barbital (N.F., Merck) of 184.5°C and mixed mp 184.5°C, [reported 176°, 183°, and 190°C for various crystal forms (*5*)]. Sodium barbital (USP, Merck) decomposed well over 200°C. Sodium content (flame, Beckman) of supernatant removed from a solution of the dried crystals that had been allowed to re-

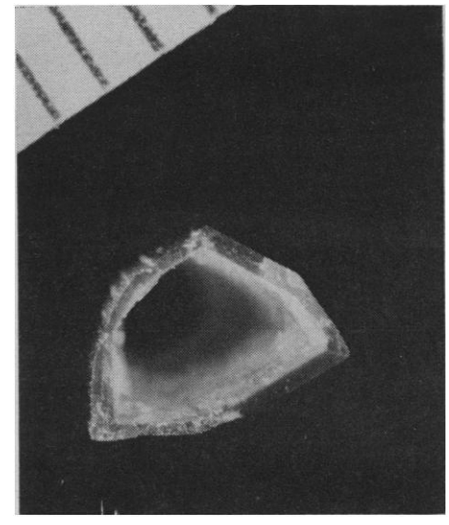

Fig. 3. Cross section of hollow crystal near open end. One scale division equals 1 mm.

crystallize (needles) overnight at room temperature showed a value of 0.3 percent of that expected for a saturated solution of sodium barbital at 25°C. This supernatant had a *p*H of 5.7 ± 0.05 and after evaporation was found to contain 0.77 ± 0.05 gm of solute per 100 ml (solubility of 5,5′-diethyl barbituric acid = 0.69 gm/100 ml at 25°C; of sodium 5,5′-diethyl barbiturate = 20.0 gm/100 ml at 25°C). It is quite possible, therefore, that the hollow crystals are simply monomeric 5,5′-diethyl barbituric acid.

Crystals were grown once before in a similar buffer solution at *p*H 8.6 ± 0.05. Also, four times they have been grown in a matter of days by seeding with very small crystal fragments (*7*).

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7. This information was presented at the meeting of the American Society of Biological Chemists, Atlantic City, April 1959. This investigation was supported by the Milton M. Frank Foundation, the Noxzema Corporation, and the Walter H. Hick Fund.

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