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The Structure of the Salt Sodium Calcium Metaphosphate ($Na_4CaP_6O_{18}$)

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In the phase diagram for the $Ca(PO_3)_2$–$NaPO_3$ system Morey[1] reports the existence of a stable sodium calcium metaphosphate, $Na_4CaP_6O_{18}$, which melts congruently at 738°. The melting characteristics and the empirical formula of the salt suggest the possibility that the salt is a true hexametaphosphate. It previously has been shown, however, that the empirical formula and the structural formula of a double salt of a metaphosphate, although related, are not necessarily the same.[2]

A salt of the composition reported by Morey was prepared by mixing 252 g. of monocalcium phosphate monohydrate, $Ca(H_2PO_4)_2 \cdot H_2O$, with 408 g. of sodium trimetaphosphate and heating the mixture to 900° for 2 hr. The salt was allowed to crystallize at 650°.

The product is a white crystalline substance which is very slowly soluble in water. All attempts to rapidly dissolve the salt by the diverse ion influence, the addition of sodium, potassium, or ammonium salts, proved fruitless. Many of the insoluble alkali metal metaphosphates respond rapidly to diverse ion treatments to yield clear solutions.

The compound in question was converted to the sodium salt by treatment of an aqueous slurry of the salt with the sodium form of a Dowex-50WX4 ion-exchange resin. When dissolved, the sodium salt was precipitated from solution with acetone and air-dried. The X-ray powder pattern of the salt was the same as that of sodium trimetaphosphate monohydrate.

Since the yield from the above conversion was rather low, a second sample was converted to the sodium salt with the same ion-exchange resin, but an excess of sodium hydroxide was added to the slurry to raise the pH of the system to a value near 12. In 12 hr. most of the phosphate had dissolved and the sodium salt again was precipitated from solution with acetone. An air-dried sample of the salt was analyzed by X-ray and was found to be sodium tripolyphosphate hexahydrate—the hydrolysis product of sodium trimetaphosphate when exposed to strongly basic solutions.[3]

The double salt $Na_4CaP_6O_{18}$ reported by Morey is a trimetaphosphate and has little or none of the sequestering influence Morey indicated he expected. This happens because trimetaphosphate is a ring compound, whereas the misnamed "metaphosphates" which exhibit sequestration of alkaline earth ions are chain compounds and really belong to the polyphosphate system and not the metaphosphate system.

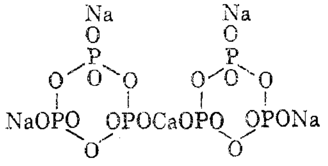
In order to erase any doubt as to the structure of the anion of the salt, $Na_4CaO_6O_{18}$, the salt was prepared from aqueous solution by dissolving sodium trimetaphosphate and calcium chloride in the correct ratios to yield the salt.

$$CaCl_2 + 2Na_3P_3O_9 \longrightarrow Na_4CaP_6O_{18} + 2NaCl$$

Crystallization was induced by the addition of a small quantity of acetone into the aqueous solution. The salt was dried at 110° and analyzed by X-ray. The powder pattern was similar to the pattern exhibited by the calcium–sodium metaphosphate prepared in the furnace. The salt prepared from aqueous solution dissolves in water much more rapidly than the salt prepared in the furnace, however. This is interpreted to mean that both salts are soluble in water but that the salt prepared in the furnace dissolves very slowly.

It is impossible to determine how the cations Ca^{++} and Na^+ are distributed in the crystal lattice of the salt from the above work.

The phosphate anion is not a hexametaphosphate but the more common trimetaphosphate and may be represented as



where one calcium ion is shared with two trimetaphosphate anions.

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[1] G. W. Morey, *J. Am. Chem. Soc.*, **74**, 5783 (1952).

[2] E. J. Griffith and J. R. Van Wazer, *ibid.*, **77**, 4222 (1955).

[3] G. B. Hatch, U. S. Patent 2,365,190 (1944).