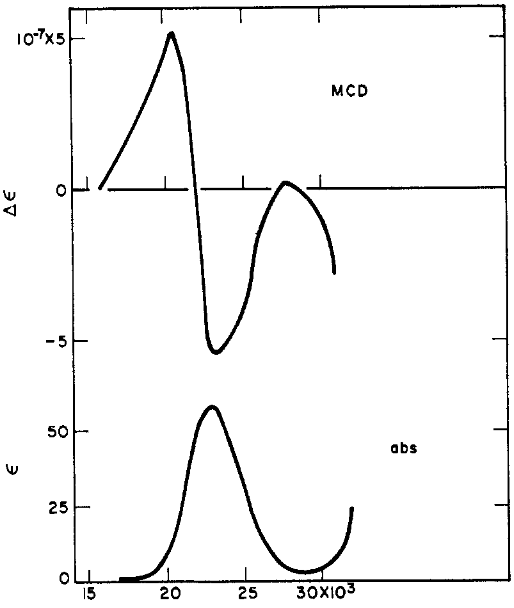

Figure 4.—MCD and absorption spectra of $[Ni(C_{10}H_{24}N_4)][ZnCl_4]$ in water.

pared as described by MacDermott and Busch[15] and the spectra were obtained from a water solution.

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On the Stoichiometry of Trisodium Orthophosphate Dodecahydrate

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Excess sodium hydroxide in trisodium orthophosphate dodecahydrate, $Na_3PO_4 \cdot 12H_2O$, and the isomorphous arsenate, vanadate, and manganate compounds has been reported repeatedly. Menzel and his collaborators[1-3] showed that pure $Na_3XO_4 \cdot 12H_2O$ (X = P, As, V) cannot be crystallized from a solution containing the stoichiometric ratio $Na_2O:X_2O_5 = 3:1$. Solutions with $Na_2O:X_2O_5$ ratios from about 2.6:1 up to 9:1 yielded crystals with $Na_2O:X_2O_5$ ratios between 3.01:1 and 3.25:1. A ratio higher than 3.25:1 was never observed by these workers and they assumed this to be a limiting composition. Their analytical results did not allow them to distinguish between water contents of 11.75 mol of H_2O or 12 mol of H_2O. In the first case NaOH would be substituted for water molecules; in the second case it would be included in the dodecahydrate structure. Menzel, *et al.*, called these compounds ψ-12-hydrates (ψ for pseudo) to distinguish them from the stoichiometric compositions, which could be obtained only from the hydration of lower hydrates, but never were found to be in equilibrium with their solutions. Serebrennikova[4] claimed that the limiting ratio for these compounds is $Na_2O:X_2O_5 = 3.33:1$ and drew an analogy to the structure of hydroxide apatite. Lux, *et al.*,[5] investigated the corresponding sodium manganate ψ-12-hydrate and suggested $Na_3MnO_4(NaOH)_{0.25}(H_2O)_{12}$ as the limiting composition. However, they stated that their analyses are not sufficiently accurate to exclude beyond all doubt the composition $Na_3MnO_4(NaOH)_{0.25}(H_2O)_{11.75}$. Bell[6] described the compound as a complex with the formula $n(Na_3PO_4 \cdot xH_2O) \cdot NaY$ where $n = 4$ or 7, $x = 11$ or 12, and Y^- is a monovalent anion such as OH^-, MnO_4^-, OCl^-, or NO_3^-. Quimby[7] reported the formula $Na_3PO_4 \cdot xNaOH \cdot (12 - x)H_2O$ with x varying between 0.1 and 0.25. Chrétien and Lelong[8] claimed that the compound $Na_3VO_4 \cdot 0.25NaOH \cdot 12H_2O$ is a complex formed by trisodium orthovanadate and sodium hydroxide tetrahydrate.

A recent determination of the crystal structure of trisodium orthophosphate dodecahydrate undertaken during a study of the crystal chemistry of hydrated sodium phosphates, arsenates, and vanadates[9] has clarified the manner in which the sodium hydroxide is built into the crystal structure of the $Na_3XO_4 \cdot 12H_2O$ salts.

Experimental Section

Crystal data are in close agreement with those of Clark and Gross:[10] $a = 11.890$ (6) Å, $c = 12.671$ (7) Å, $V = 1551$ (3) Å³, space group $P\bar{3}c1$, $Z = 4$, $d_x = 1.65$ g/cm³, $d_m = 1.64$ g/cm³. The unit cell constants are based on the refinement of 20 reflections which had been centered on an automatic four-angle X-ray diffractometer. Systematic extinctions ($h\bar{h}0l$ only with $l = 2n$) are consistent with space groups $P\bar{3}c1$ and $P3c1$; the centric space group was confirmed by the successful refinement of the structure. The crystal used for the structure determination was commercial sodium phosphate (tribasic crystal, Baker 3836) which contained an excess of 0.155 mol of NaOH per formula unit $Na_3PO_4 \cdot 12H_2O$ according to a company analysis. The crystal structure was determined by three-dimensional Patterson and Fourier methods and refined to $R = 0.056$ for 556 observed F_{hkl}.

Results and Discussion

The prominent structural unit is a two-dimensionally infinite sheet of $Na(OH_2)_6$ coordination octahedra with a composition $Na(OH_2)_4$. Within one sheet the $Na(OH_2)_6$ octahedra share corners to form rings of six octahedra, with each ring connected to six other ones

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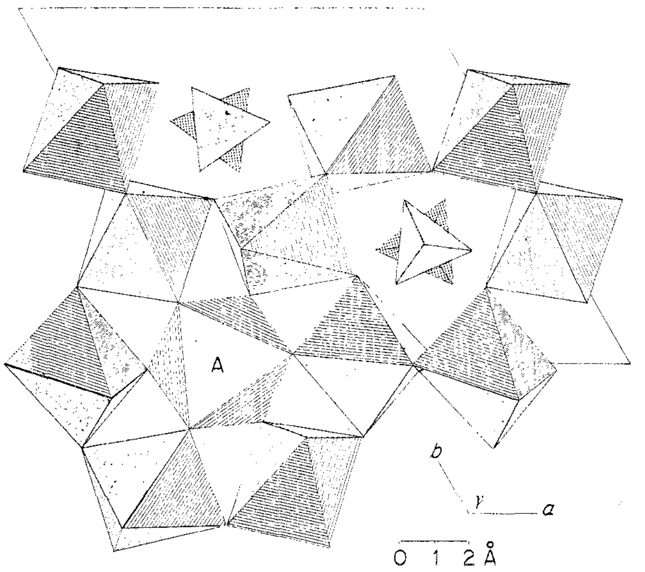

Figure 1.—[Na$_{12-13}$(OH)$_{0-1}$(OH$_2$)$_{48}$][(PO)$_4$] viewed parallel to [00.1].

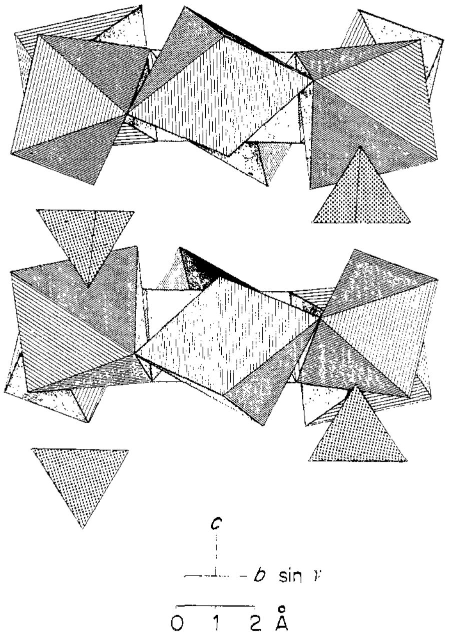

Figure 2.—[Na$_{12-13}$(OH)$_{0-1}$(OH$_2$)$_{48}$][(PO$_4$)$_4$] viewed parallel to [10.0].

via common edges (Figure 1). The only connections between two sheets are hydrogen bonds from the water molecules to the phosphate groups located between the sheets (Figure 2). It is apparent that there are large voids in the centers of the rings at 0, 0, 0 and 0, 0, $^1/_2$. These sites (A sites) correspond to a twofold special position in space group P$\bar{3}$c1 and are coordinated octahedrally by the six water molecules O(w6). This position is the only one which is available for the additional Na and OH ions. An inspection of the electron density map and a least-squares refinement of the occupancy factor of a "mixed" atom ($0.5f_{Na} + 0.5f_O$) on the A site showed that 0.64(Na, OH) are located there. This corresponds to an excess of 0.16 NaOH per formula unit $Na_3PO_4 \cdot 12H_2O$ in good agreement with the analysis. Full occupation of this position would correspond to a ratio of $Na_3PO_4 \cdot 12H_2O$:NaOH = 1:0.25.

These results confirm the earlier reports about the upper limit of NaOH excess, since not more than 0.25 mol of NaOH can occupy the A site in the structure of $Na_3PO_4 \cdot 12H_2O$. There is no apparent reason for two definite values of 0.12 and 0.21 mol of NaOH as given by Bell[6] and Wendrow and Kobe.[11] Most likely every amount of sodium hydroxide between 0 and 0.25 mol can be included in the structure depending on the conditions under which the crystal was formed. Accordingly the formula should be written [Na$_{12-13}$(OH)$_{0-1}$(OH$_2$)$_{48}$][(PO$_4$)$_4$]. The bond length O(w6)–Na is 2.61 Å, while the distance O(w6)–A is 2.44 Å. These bond lengths as well as all other ones surrounding the A position will depend on whether A is occupied by Na or OH or not occupied at all. This is characterized by the high and strongly anisotropic temperature factor of O(w6). In the last steps of the refinement process we allowed variation of the occupancy factor of O(w6); it did not change however. Highly overexposed X-ray photographs have been taken to detect any additional weak reflections. A doubling of the *c* lattice constant for example would allow an ordered distribution of Na and OH, but no evidence for this has been found.

A statistical occupation of the same site by a cation (Na^+) and by an anion (OH^-) appears to be very unusual. It seems to be made possible in this case by the flexibility of the hydrogen-bonding arrangement. If the A site is occupied by the sodium ion, the O(w6) water molecules form hydrogen bonds to neighboring water oxygen atoms. If it is occupied by an OH group, the O(w6) water molecule can donate one of its hydrogen bonds to OH^-, so that the hydroxide group can receive a maximum of six hydrogen bonds. If the A site is not occupied, the O(w6) molecules can donate one of their hydrogen bonds to their O(w6) neighbors within the coordination polyhedron around the same A site. In each of these three cases a reasonable hydrogen-bonding scheme can be constructed. A similar case has been found in $(Na_3PO_4)_2NaF \cdot 19H_2O$,[9] where a sodium atom in tetrahedral four-coordination shares statistically one site with an H_2O molecule. Again this arrangement is only made possible through the flexibility of the hydrogen-bonding scheme.

It seems possible that other anions similar in size to OH^- can be included in the crystal structure. The void around the A site, however, is not large enough to accommodate considerably larger anions such as NO_3^- and MnO_4^-. For the inclusion of these anions at least three of the twelve O(w6) molecules would have to be replaced by oxygen atoms leaving 11.25 mol of H_2O per formula unit. This is in close agreement with the value of 11 mol of H_2O given by Bell[6] for such compounds.

(11) B. Wendrow and K. A. Kobe, *Chem. Rev.*, **54**, 891 (1954).