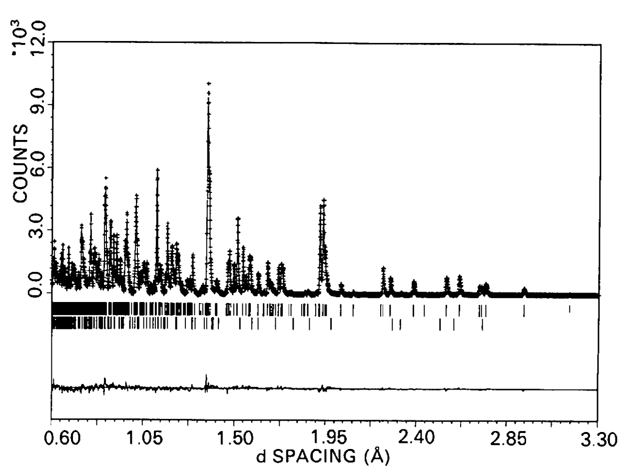

Fig. 1. Portion of the final Rietveld fit for $YBa_2Cu_4O_8$ at room temperature. Plus marks (+) represent the raw data, the solid line is the calculated profile. A difference (obs. − calc.) plot is shown beneath. The two sets of tick marks represent reflection positions for $YBa_2Cu_4O_8$ (upper) and CuO (lower).

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Structure of Trisodium Monohydroxogermanate(IV) Pentahydrate

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Abstract. $Na_3[GeO_3(OH)].5H_2O$, $M_r = 296{\cdot}6$, orthorhombic, *Pbca*, $a = 11{\cdot}889\,(6)$, $b = 11{\cdot}039\,(2)$, $c = 13{\cdot}090\,(2)$ Å, $V = 1717{\cdot}9$ Å^3, $Z = 8$, $D_m = 2{\cdot}18$, $D_x = 2{\cdot}29$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71073$ Å, $\mu = 3{\cdot}68$ mm^{-1}, $F(000) = 1128$, $T = 296$ K, $R = 0{\cdot}034$ for 1266 independent reflections. Isostructural relation established with $Na_3[SiO_3(OH)].5H_2O$. All H atoms located from ΔF map. The structure of $Na_3[GeO_3(OH)].5H_2O$ shows centrosymmetric dimeric units of hydrogen bonded $[GeO_3(OH)]^{3-}$ tetrahedra. The hydrogen bonds of the edge-sharing tetrahedra are short and strong [O1···O3 = 2·568 (3) Å]. The Na atoms show very distorted Na—O polyhedra, two Na atoms with coordination number 7 and one with coordination number 6. The face-sharing Na—O polyhedra show a wave-like extension along [001]. A coordination number of 5 is observed for all water molecules with two H and three Na atoms coordinating the O atom.

Introduction. There are a limited number of phase analogues in the series of sodium silicate and sodium germanate hydrates known so far which have the hydroxoorthoanions $[XO_{4-x}(OH)_x]^{(4-x)-}$ with X = Si,Ge, x = 1,2 in common. Four hydrate phases are known in the silicate series $Na_2[SiO_2(OH)_2].nH_2O$ with n = 4,5,7,8. Corresponding germanates show n = 5 (Jamieson & Dent Glasser, 1967) and n = 6 (Nowotny & Szekely, 1952; Bauren & Ingri, 1967; Schmid, Ketterer, Felsche & Hiller, 1988). We report here on the structure of sodium germanate pentahydrate $Na_3[GeO_3(OH)].5H_2O$ which is the first analogue known of the silicate series $Na_3[SiO_3(OH)].nH_2O$ which shows n = 5 (Smolin, Shepelev & Butikova, 1973), n = 2 (Schmid, Huttner & Felsche, 1979; Schmid, Zsolnai, Felsche & Huttner, 1980; Schmid & Felsche, 1983) and n = 1 (Schmid & Felsche, 1990).

In the context of our research program which is concerned with the mechanisms of melting or peritectical decomposition of the water-rich hydrates of oxosalts we are interested in the structural details especially in the hydrogen bonding of the phases of both series. This is because of the unique thermal properties of the dihydroxo hydrates $Na_2[SiO_2(OH)_2].nH_2O$ of the system Na_2O—SiO_2—H_2O

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which are the 'parent phases' of the waterglass materials $Na_2O.ySiO_2.nH_2O$ with $1 \le y \le 4$, $4 \le n \le 16$ as revealed from the congruent but irreversible melting and thermal decomposition characteristics (Felsche, Ketterer & Schmid, 1985). The series of monohydroxo hydrates $Na_3[XO_3(OH)].nH_2O$ ($X =$ Si,Ge) shows different melting characteristics with peritectical decomposition (Schmid & Felsche, 1983). The different melting properties in the two series are well correlated to the different schemes of hydrogen bonding and packing of the $Na(O,OH,OH_2)_y$ coordination polyhedra with $5 \le y \le 7$ and the oxoanions $[XO_{4-x}(OH)_x]^{(4-x)-}$ with $X =$ Si,Ge and $x = 1,2$ in the corrresponding structures as shown by neutron diffraction studies (Williams & Dent-Glasser, 1971; Schmid, Felsche & McIntyre, 1984, 1985).

Experimental. Single crystals of $Na_3[GeO_3(OH)].5H_2O$ were obtained by isothermal crystal growth from supersaturated aqueous solutions containing 18·4% Na_2O, 3·5% GeO_2 and 78·1% H_2O (by weight) by the evaporation method in a CO_2-free box. For X-ray investigations a prismatic crystal of dimensions 0·3 × 0·3 × 0·3 mm was sealed in a glass capillary because of the hygroscopic character of the given species. D_m was measured by flotation.

Enraf–Nonius CAD-4 diffractometer, graphite monochromator, lattice constants from 25 reflections with $3 < \theta < 18°$. Variable $\omega/2\theta$-scan technique, 1967 reflections measured totally up to $(\sin\theta)/\lambda = 0{\cdot}595$ Å^{-1} in the hemisphere $0 \le h \le 14$, $0 \le k \le 13$, $0 \le l \le 15$ (some of the reflections also measured in the hemisphere $-14 \le h \le 0$, $-13 \le k \le 0$, $0 \le l \le 15$). Three standard reflections showed only small random variations during the measurements. Empirical absorption correction, minimum and maximum relative transmission factors 70·78 and 99·95%, respectively. 1507 unique reflections after merging equivalent reflections ($R_{\rm int} = 0{\cdot}038$), 241 reflections considered unobserved [$I < 2{\cdot}0\sigma(I)$] and excluded from structure refinement.

Heavy-atom method, full-matrix least-squares refinements, function minimized $\sum w(\Delta F)^2$, 1266 observed reflections weighted according to $w = 4F^2/[\sigma^2(I) + (0{\cdot}04F^2)^2]$. All H atoms located in difference Fourier synthesis. In final refinement 118 parameters varied: one overall scale factor as well as coordinates and anisotropic displacement parameters of all non-H atoms; coordinates and arbitrary isotropic displacement parameters of the H atoms kept fixed. $R = 0{\cdot}034$, $wR = 0{\cdot}064$, $S = 2{\cdot}411$. Maximum Δ/σ in last cycle 0·02. Minimum and maximum $\Delta\rho$ in final ΔF map $-0{\cdot}71$ and $+0{\cdot}59$ e Å^{-3}, respectively, near Ge atom. Complex atomic scattering factors taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations performed on a VAX 3200 computer (Digital Equipment) using the Enraf–Nonius (1989) *SDP* program system, drawings generated with the program *ORTEP*II (Johnson, 1976).

Table 1. *Fractional atomic coordinates and isotropic displacement parameters* (Å^2) *with e.s.d.'s in parentheses*

Coordinates of the H atoms taken from ΔF map have not been refined.

$$B = \textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	B
Ge	0·47802 (5)	0·62588 (5)	0·62966 (4)	1·12 (1)
Na1	0·3251 (2)	0·6339 (2)	0·3699 (2)	1·51 (4)
Na2	0·1831 (2)	0·6080 (2)	0·5815 (2)	1·59 (4)
Na3	0·3361 (2)	0·3756 (2)	0·6776 (2)	1·74 (4)
O1	0·3713 (3)	0·5429 (3)	0·5666 (3)	1·30 (7)
O2	0·4665 (3)	0·7732 (3)	0·5890 (3)	1·10 (7)
O3	0·6085 (3)	0·5688 (3)	0·6045 (3)	1·14 (7)
O4	0·4436 (3)	0·6007 (3)	0·7556 (3)	1·65 (7)
O5	0·3619 (3)	0·5589 (3)	0·1910 (3)	1·60 (7)
O6	0·2365 (3)	0·6983 (3)	0·7574 (3)	1·51 (7)
O7	0·2521 (4)	0·7178 (3)	0·0071 (3)	1·89 (8)
O8	0·5140 (3)	0·7410 (4)	0·3851 (3)	1·90 (8)
O9	0·3635 (3)	0·4295 (4)	0·8920 (3)	2·37 (9)
H1	0·385	0·500	0·514	4
H51	0·418	0·516	0·221	4
H52	0·400	0·616	0·166	4
H61	0·201	0·650	0·805	4
H62	0·301	0·668	0·764	4
H71	0·318	0·699	0·027	4
H72	0·217	0·668	−0·029	4
H81	0·500	0·768	0·459	4
H82	0·484	0·799	0·346	4
H91	0·416	0·385	0·902	4
H92	0·383	0·500	0·859	4

Discussion. The final atomic parameters for $Na_3[GeO_3(OH)].5H_2O$ are listed in Table 1.* Bond lengths and angles observed in the hydrogen-bonding system and in the cation oxygen coordinations are listed in Table 2. The results imply an isostructural relation with the silicate $Na_3[SiO_3(OH)].5H_2O$ (Smolin, Shepelev & Butikova, 1973). Significant differences between the two hydrate structures arise from the longer bond lengths in the germanate hydroxoanion: Ge—OH = 1·769 (2), Si—OH = 1·677 (2) Å; mean Ge—O = 1·728, mean Si—O = 1·621 Å. Angles O—Ge—O are considerably larger than the O—Ge—OH angles which show mean values of 112·3 and 106·6°, respectively. Similar relations have been observed in the corresponding silicate anion $[SiO_3(OH)]^{3-}$ and also in the pair of isostructural hydrates $Na_2[GeO_2(OH)_2].5H_2O$ and $Na_2[SiO_2(OH)_2].5H_2O$ (Jamieson & Dent-Glasser, 1967).

The most outstanding structural feature is the bitetrahedral grouping of the individual $[GeO_3-$

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* Lists of the anisotropic displacement parameters of the non-H atoms, the bond angles in the Na—O polyhedra, and the structure factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53868 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

$[GeO_3(OH)]^{3-}$ tetrahedron

Ge—O1	1·769 (2)	Ge—O4	1·720 (2)
Ge—O2	1·716 (2)	O1—H1	0·85
Ge—O3	1·707 (2)		
O1—Ge—O2	106·8 (1)	O2—Ge—O4	115·5 (1)
O1—Ge—O3	111·8 (1)	O3—Ge—O4	110·0 (1)
O1—Ge—O4	101·1 (1)	Ge—O1—H1	122
O2—Ge—O3	111·3 (1)		

Na—O polyhedra

Na1—O1	2·818 (3)	Na2—O1	2·360 (3)	Na3—O1	2·386 (3)
Na1—O3′	2·396 (3)	Na2—O5′	2·394 (3)	Na3—O4	2·975 (3)
Na1—O5	2·521 (3)	Na2—O6	2·588 (3)	Na3—O5′	2·470 (3)
Na1—O6′	2·590 (3)	Na2—O7′	2·306 (3)	Na3—O6′	2·381 (3)
Na1—O7′	2·580 (3)	Na2—O8′	2·648 (3)	Na3—O7′	2·672 (3)
Na1—O8	2·547 (3)	Na2—O9′	2·574 (3)	Na3—O8′	2·347 (3)
Na1—O9′	2·368 (3)			Na3—O9	2·887 (3)

H_2O molecules

O5—H51	0·90	O7—H71	0·85
O5—H52	0·84	O7—H72	0·83
O6—H61	0·92	O8—H81	1·02
O6—H62	0·84	O8—H82	0·89
O9—H92	0·91	O9—H91	0·80
H51—O5—H52	99	H81—O8—H82	105
H61—O6—H62	96	H91—O9—H92	113
H71—O7—H72	118		

Hydrogen bonds

O1···O3′	2·568 (3)	H1···O3′	1·72	O1—H1···O3′	168
O5···O4′	2·986 (3)	H51···O4′	2·11	O5—H51···O4′	162
O5···O2′	2·595 (3)	H52···O2′	1·77	O5—H52···O2′	167
O6···O3′	2·759 (3)	H61···O3′	1·84	O6—H61···O3′	170
O6···O4	2·682 (3)	H62···O4	1·85	O6—H62···O4	170
O7···O2′	2·770 (3)	H71···O2′	1·96	O7—H71···O2′	156
O7···O3′	2·781 (3)	H72···O3′	1·95	O7—H72···O3′	168
O8···O2	2·743 (3)	H81···O2	1·74	O8—H81···O2	164
O8···O4′	2·572 (3)	H82···O4′	1·68	O8—H82···O4′	169
O9···O2′	2·669 (3)	H91···O2′	1·86	O9—H91···O2′	173
O9···O4	2·768 (3)	H92···O4	1·89	O9—H92···O4	158

A prime indicates an atomic position which is symmetry equivalent with that of the same number given in Table 1.

$(OH)]^{3-}$ tetrahedra *via* edge-sharing hydrogen bonding as shown in Fig. 1. Short donor–acceptor distances of O1···O3 = 2·568 (3) Å indicate strong hydrogen bonds. The nearly closest packing of the centrosymmetric bitetrahedra $[O_2GeOOH\cdots OHOGeO_2]^{6-}$ is emphazised in Fig. 2(*b*). The distortion from cubic to orthorhombic symmetry is caused by the alignment of the bitetrahedra showing the largest dimension along [001]. Wavy chains of face sharing Na—O polyhedra also follow this direction [Fig. 2(*a*)]. Interconnection of the chains along [010] is given by edge sharing and along [100] by corner sharing with every fourth atom in the chain of the Na—O coordination polyhedra. The degree of distortion in the coordination of the Na atoms even exceeds the data reported for the isostructural silicate (Smolin, Shepelev & Butikova, 1973). The bond-length variation is largest in the two sevenfold coordinated Na atoms which show values of 2·368 (3) ≤ Na1—O ≤ 2·818 (3) Å and 2·347 (3) ≤ Na3—O ≤ 2·975 (3) Å.

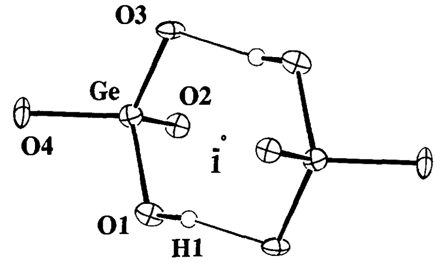

Fig. 1. Configuration of the monohydroxoorthogermanate anion $[GeO_3(OH)]^{3-}$ in the bitetrahedral grouping $[O_2GeOOH\cdots OHOGeO_2]^{6-}$.

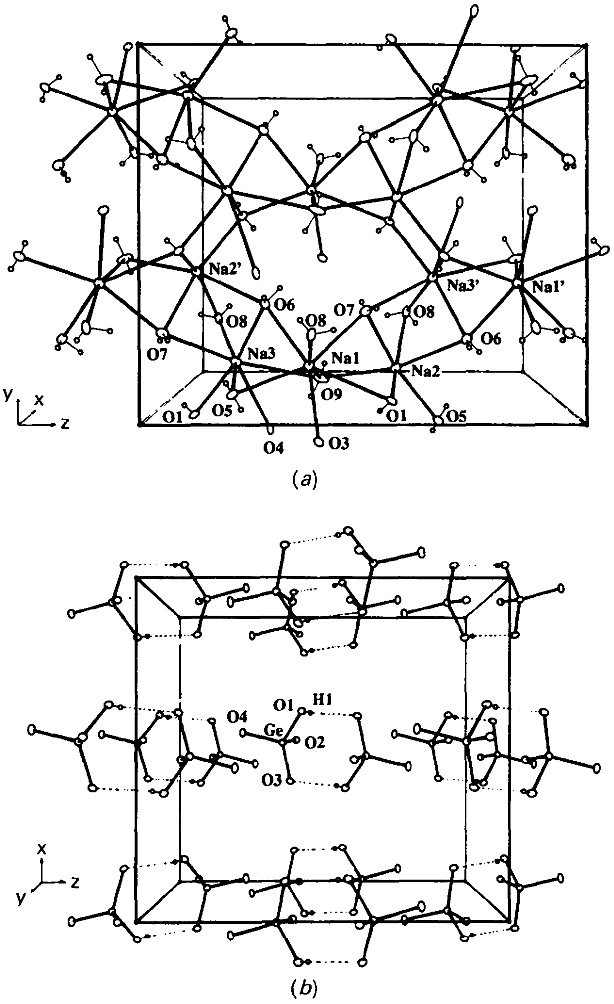

Fig. 2. (*a*) Configuration and interlinkage of the Na—O coordination polyhedra, view along [100]. (*b*) Packing of the bitetrahedral groupings $[O_2GeOOH\cdots OHOGeO_2]^{6-}$, view along [010].

The discussion of the hydrogen bonding in the structure of $Na_3[GeO_3(OH)].5H_2O$ by means of the data in Table 2 suffers from the well known problem of systematic shortening of O—H distances (and systematic lengthening of H···O distances) due to the character of X-ray scattering. The coordination of the H_2O molecules is of type *O* class 3 according to the classification of Ferraris & Franchini-Angela (1972) and Chiari & Ferraris (1982) with significant fivefold coordination of all O atoms O5 to O9. The hydrogen-bonding scheme challenges the verification by neutron diffraction. Corresponding experiments are planned.

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Crystal Chemistry of *cyclo*-Hexaphosphates. XI. Structure of Ammonium Copper *cyclo*-Hexaphosphate Octahydrate

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Abstract. $Cu_2(NH_4)_2(P_6O_{18}).8H_2O$, $M_r = 781{\cdot}033$, triclinic, $P\bar{1}$, $a = 7{\cdot}413\,(3)$, $b = 9{\cdot}334\,(4)$, $c = 9{\cdot}634\,(4)$ Å, $\alpha = 116{\cdot}23\,(5)$, $\beta = 107{\cdot}98\,(5)$, $\gamma = 83{\cdot}10°$, $V = 569\,(1)$ Å^3, $Z = 1$, $D_x = 2{\cdot}280$ Mg m^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}7107$ Å, $\mu = 2{\cdot}280$ mm^{-1}, $F(000) = 394$, $T = 294$ K, final $R = 0{\cdot}030$ for 2293 reflections. The P_6O_{18} ring anions and the distorted CuO_6 octahedra form a two-dimensional network parallel to the *bc* plane. These layers are interconnected in a three-dimensional manner by the $(NH_4)O_8$ polyhedra and the hydrogen-bond network.

Introduction. Several divalent–monovalent cation *cyclo*-hexaphosphates have already been described by the authors: $Mn_2Li_2(P_6O_{18}).10H_2O$ (Averbuch-Pouchot, 1989), $Cd_2Na_2(P_6O_{18}).14H_2O$ (Averbuch-Pouchot, 1990), $Ca_2Li_2(P_6O_{18}).8H_2O$ and its isotype, the corresponding calcium–sodium salt (Averbuch-Pouchot & Durif, 1990). In the present work we describe the chemical preparation and crystal structure of ammonium copper *cyclo*-hexaphosphate octahydrate, $Cu_2(NH_4)_2(P_6O_{18}).8H_2O$.

Experimental. Crystals of the title compound have been prepared by using an almost saturated aqueous solution of ammonium *cyclo*-hexaphosphate, added with the stoichiometric amount of a copper hydroxycarbonate $[CuCO_3.Cu(OH)_2]$. In this slurry, drops of concentrated hydrochloric acid were added until the copper hydroxycarbonate disappeared. Crystals of $Cu_2(NH_4)_2(P_6O_{18}).8H_2O$ appear immediately as diamond-like plates. Polycrystalline samples can be prepared by slow evaporation at room temperature of an aqueous solution of copper chloride and ammonium *cyclo*-hexaphosphate corresponding to the stoichiometry $CuCl_2/(NH_4)_6(P_6O_{18}) = 3$. This salt is very sparingly water soluble.

Crystal size: $0{\cdot}19 \times 0{\cdot}19 \times 0{\cdot}10$ mm (a diamond-like plate). Density not measured. Philips PW1100 diffractometer, graphite monochromator. 15 reflections ($10 < \theta < 17°$) for refining unit-cell dimensions. ω scan, scan width: 1·20°, scan speed: $0{\cdot}02°\ s^{-1}$, total background measuring time: 6 s. 2651 reflections collected ($3 < \theta < 30°$), $\pm h$, $\pm k$, l, $h_{max} = 10$, $k_{max} = 12$, $l_{max} = 13$. Two orientation and intensity control

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