O(45$^i$), *i.e.* binds different anions in the [001] direction. It is also an acceptor of hydrogen bonds from Aq(26) and Aq(34). The coordination of O atoms around Aq(1) is tetrahedral with distances as given in Table 6.

### The disordered water molecule

Aq(13) is, as previously mentioned, disordered over two positions with occupancy factors 0·363 (13) and 0·637 (13) for positions *a* and *b* respectively. A possible explanation for this is the formation of different weak hydrogen bonds for the two positions, in which Aq(13) acts as a donor, see Table 6. Na(1) and Na(3) complete a tetrahedral arrangement of atoms around Aq(13) in both the *a* and *b* positions.

### References

ANTTI, B.-M. (1976). *Acta Chem. Scand.* A30, 24–30.
COPPENS, P. & HAMILTON, W. C. (1970). *Acta Cryst.* A26, 71–83.
HEDMAN, B. (1973). *Acta Chem. Scand.* 27, 3335–3354.
HEDMAN, B. (1977). *Acta Cryst.* B33, 3077–3083.
HEDMAN, B. & STRANDBERG, R. (1977). To be published.
*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 71–98, 149. Birmingham: Kynoch Press.
JOHANSSON, G., PETTERSSON, L. & INGRI, N. (1974). *Acta Chem. Scand.* A28, 1119–1128.
JOHNSON, C. K. (1965). *ORTEP.* Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
PETTERSSON, L. (1974). Dissertation, Univ. of Umeå.
PETTERSSON, L. (1975). *Chem. Scripta*, 7, 145–154.
STRANDBERG, R. (1973). *Acta Chem. Scand.* 27, 1004–1018.
STRANDBERG, R. (1974). *Acta Chem. Scand.* A28, 217–225.
STRANDBERG, R. (1975a). *Acta Chem. Scand.* A29, 350–358.
STRANDBERG, R. (1975b). *Acta Chem. Scand.* A29, 359–364.
WERNER, P.-E. (1969). *Ark. Kem.* 31, 513–516.

# Multicomponent Polyanions.
# 17. The Crystal Structure of Na₄Mo₁₂GeO₄₀(H₂O)₈, a Compound Containing Sodium-Coordinated Dodecamolybdogermanate Anions

BY ROLF STRANDBERG

*Department of Inorganic Chemistry, University of Umeå, S-901 87 Umeå, Sweden*

The crystal structure of Na₄Mo₁₂GeO₄₀(H₂O)₈ has been determined from three-dimensional X-ray diffraction data collected with a Pailred diffractometer using Mo $K\alpha$ radiation. There are two formula units in the triclinic ($P\bar{1}$) unit cell and the cell parameters are $a = 14\cdot421$ (1), $b = 13\cdot187$ (1), $c = 11\cdot596$ (1) Å, $\alpha = 114\cdot31$ (1), $\beta = 103\cdot88$ (1) and $\gamma = 76\cdot45$ (1)°. The structure was refined by least-squares methods using anisotropic vibrational parameters to a final $R$ value of 0·029 based on 9988 independent reflexions. The structure is built up of Mo₁₂GeO₄₀⁴⁻ groups linked together by Na⁺ and water molecules in a three-dimensional framework. The heteropolyanion has the well known Keggin structure ($\alpha$ isomer). The Mo–Mo distances within the group vary between 3·32 and 3·38 Å when the MoO₆ octahedra are sharing edges and increase to 3·70–3·78 Å when only a corner is shared. As would be expected from previous investigations, the Mo–O distances depend on the O coordination number. The four groups of Mo–O distances observed have mean values of 1·69, 1·82, 2·05 and 2·29 Å.

### Introduction

The present crystal structure study forms part of a research project in progress in this department aimed at elucidating the equilibria and structures of three-component polyanion complexes present in aqueous solutions. One of the systems studied contains the reacting components H⁺, MoO₄²⁻ and Ge(OH)₄. The

equilibria involved when the three-component complexes are formed may be written in the general form

$$p\mathrm{H^+} + q\mathrm{MoO_4^{2-}} + r\mathrm{Ge(OH)_4} \rightleftharpoons$$
$$(\mathrm{H^+})_p(\mathrm{MoO_4^{2-}})_q[\mathrm{Ge(OH)_4}]_r,$$
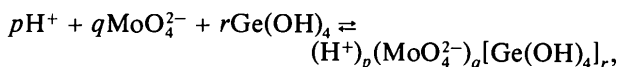
where $p$, $q$ and $r$ are integers defining the complexes. The equilibrium analyses indicate the presence of complexes with $q:r$ ratios of 6:1, 9:1 and/or 12:1.

In this system, five crystalline phases have been obtained from equilibrium solutions as well as from crystallization experiments. The equilibrium investigations give only the compositions $[(p,q,r)]$ and formation constants $(\beta_{pqr})$ of the complexes formed. In order to obtain structural information, investigations of crystalline phases, by means of X-ray diffraction, may be performed. In the present paper the results of such an investigation are reported. The $(p,q,r)$ notation for the complex studied is (20,12,1).

## Experimental

### Crystal preparation

In a typical preparation of the crystals, $\mathrm{GeO_2}$, $\mathrm{Na_2MoO_4 \cdot 2H_2O}$ and $\mathrm{NaClO_4}$ were dissolved in dilute $\mathrm{HClO_4}$ to the concentrations $[\mathrm{MoO_4^{2-}}]_{tot} = 120$ m$M$, $[\mathrm{Ge(OH)_4}]_{tot} = 20$ m$M$, $[\mathrm{HClO_4}]_{tot} = 206$ m$M$ and $[\mathrm{NaClO_4}]_{tot} = 3 \cdot 0$ $M$. The dissolution of $\mathrm{GeO_2}$ was carried out according to Ingri (1963). The solution was allowed to stand at room temperature for slow evaporation. After a few days, sea-green prismatic crystals were obtained. The crystals are stable in air.

### Crystal data

A number of crystals were mounted and Weissenberg photographs (rotation and zero-level) were recorded. Only the diffraction symmetry $\bar{1}$ could be observed, which determined the crystal system as triclinic. Preliminary cell parameters were calculated from Weissenberg and precession photographs recorded from the crystal used in the data collection. Accurate cell dimensions were refined from a powder photograph recorded with a Guinier–Hägg camera and with $\mathrm{Pb(NO_3)_2}$ ($a = 7 \cdot 8575$ Å, 25°C) as internal standard. The crystal data are: $\mathrm{Na_4Mo_{12}GeO_{40}(H_2O)_8}$, FW 2099·9, triclinic, $P\bar{1}$, $a = 14 \cdot 421$ (1), $b = 13 \cdot 187$ (1), $c = 11 \cdot 596$ (1) Å, $\alpha = 114 \cdot 31$ (1), $\beta = 103 \cdot 88$ (1), $\gamma = 76 \cdot 45$ (1)°, $V = 1928$ Å$^3$, $Z = 2$, $D_x = 3 \cdot 62$ g cm$^{-3}$, $\mu(\mathrm{Mo}\,K\alpha) = 46 \cdot 2$ cm$^{-1}$.

### Collection of intensity data

Three-dimensional intensity data were collected at 25 °C with a Philips Pailred linear diffractometer using Mo $K\alpha$ radiation. A crystal of approximate dimensions $0 \cdot 11 \times 0 \cdot 11 \times 0 \cdot 17$ mm was mounted and rotated about the $c$ axis (parallel to the $0 \cdot 17$ mm edge of the

crystal). 11490 reflexions from the layers $hk0$–$hk13$ up to a limit of $(\sin\theta)/\lambda \sim 0 \cdot 75$ Å$^{-1}$ were scanned. Reflexions with a relative statistical error $\Delta I_o/I_o$ (Antti, 1973) greater than $0 \cdot 5$ were omitted; this reduced the number of unique observed reflexions to 9988. The intensities were corrected for Lorentz and polarization effects and an absorption correction was applied.

## Structure determination and refinement

The centrosymmetric space group $P\bar{1}$ was chosen and the structure determination successfully completed with this space group. From a three-dimensional Patterson synthesis the positions of the Ge and Mo atoms were found. Three-dimensional Fourier syntheses gave the coordinates of the remaining O and Na atoms. There were no difficulties in distinguishing water O atoms and Na atoms since the latter had negative isotropic thermal parameters when refined with the scattering factors for O$^-$.

The positional parameters and anisotropic temperature factors for the atoms were refined by full-matrix least-squares methods and the final $R$ value was $0 \cdot 029$ (where $R = \Sigma \|F_o\| - |F_c\|/\Sigma |F_o|$). The atomic scattering factors used for Mo$^{3+}$, Ge, O$^-$ and Na$^+$ were those given in International Tables for X-ray Crystallography (1974). Account was taken of the real part of the dispersion correction. A weighting scheme according to Cruickshank (1965) was applied; $w = 1/(a + |F_o| + c|F_o|^2 + d|F_o|^3)$, where the values of the constants were $a = 500$, $c = 0 \cdot 001$ and $d = 0 \cdot 00003$. The final difference Fourier synthesis showed no anomalies.

The computer programs used have been described by Antti (1976), and the computations were performed with the CD 3300 and CD CYBER 172 computers at the University of Umeå.

Final positional parameters are given in Table 1.*

## Description and discussion of the structure

The crystal structure is built up of $\mathrm{Mo_{12}GeO_{40}^{4-}}$ anions joined in a three-dimensional framework by Na$^+$ ions and water molecules. The connexions comprise O–Na–O and O–Na–Aq–Na–O bridges as well as numerous hydrogen bonds.

### The $\mathrm{Mo_{12}GeO_{40}}$ group

The group consists of a central $\mathrm{GeO_4}$ tetrahedron whose O atoms are part of the surrounding twelve

---

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32596 (39 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates* ($\times 10^4$; *for* Mo *and* Ge $\times 10^5$)

Estimated standard deviations are given in parentheses. For the O atoms O($i$), O($i,j$) and OGe($i,j,k$) the index means that the atom is bonded to Mo atoms $i$ (and $j$, $k$) and Ge indicates that it is also bonded to the Ge atom. Aq($i$) and Aq($i,j$) denote water O atoms coordinated to Na$^+$ ions $i$ (and $j$).

|  | $x$ | $y$ | $z$ |
|---|---|---|---|
| Ge | 25461 (3) | 24614 (4) | 25941 (5) |
| Mo(1) | 22610 (3) | 30129 (3) | 57475 (4) |
| Mo(2) | 45095 (3) | 27869 (3) | 51848 (4) |
| Mo(3) | 28690 (3) | 50439 (3) | 51965 (4) |
| Mo(4) | 1624 (3) | 32314 (3) | 32084 (4) |
| Mo(5) | 15953 (3) | 4163 (3) | 29699 (4) |
| Mo(6) | 39624 (3) | −213 (3) | 28292 (4) |
| Mo(7) | 48870 (3) | 17976 (3) | 17840 (4) |
| Mo(8) | 36181 (3) | 43326 (3) | 20545 (4) |
| Mo(9) | 9839 (3) | 48554 (3) | 22509 (4) |
| Mo(10) | 4803 (3) | 23038 (3) | 1545 (4) |
| Mo(11) | 22939 (3) | 97502 (3) | 1695 (4) |
| Mo(12) | 29795 (3) | 20136 (3) | 95504 (4) |
| O(1) | 1831 (3) | 3207 (3) | 7054 (4) |
| O(1,2) | 3581 (2) | 2774 (3) | 6261 (3) |
| O(1,3) | 2379 (2) | 4663 (3) | 6253 (3) |
| O(1,4) | 1022 (2) | 3455 (3) | 4672 (3) |
| O(1,5) | 2095 (3) | 1582 (3) | 4696 (3) |
| OGe(1,2,3) | 2930 (2) | 3136 (3) | 4217 (3) |
| O(2) | 5540 (2) | 2589 (3) | 6191 (3) |
| O(2,3) | 4193 (2) | 4320 (3) | 5808 (3) |
| O(2,6) | 4250 (2) | 1159 (3) | 4264 (3) |
| O(2,7) | 4897 (2) | 2562 (3) | 3728 (3) |
| O(3) | 6994 (3) | 3604 (3) | 3902 (4) |
| O(3,8) | 3557 (2) | 4823 (3) | 3730 (3) |
| O(3,9) | 8221 (2) | 4856 (3) | 5957 (3) |
| O(4) | 9087 (3) | 3244 (3) | 3571 (4) |
| O(4,5) | 663 (2) | 1564 (3) | 2821 (3) |
| O(4,9) | 19 (2) | 4588 (3) | 3085 (3) |
| O(4,10) | 9637 (2) | 2611 (3) | 1253 (3) |
| OGe(4,9,10) | 1365 (2) | 3042 (2) | 2163 (3) |
| O(5) | 8923 (3) | 250 (3) | 6433 (4) |
| O(5,6) | 7036 (2) | 384 (3) | 6719 (3) |
| O(5,11) | 8474 (2) | 498 (3) | 8724 (3) |
| OGe(5,6,11) | 2580 (3) | 1051 (3) | 2245 (3) |
| O(6) | 5138 (3) | 1084 (3) | 7118 (4) |
| O(6,7) | 4521 (3) | 648 (3) | 1944 (4) |
| O(6,11) | 6632 (3) | 914 (3) | 9053 (4) |
| O(7) | 6100 (3) | 1464 (3) | 1865 (4) |
| O(7,8) | 4805 (3) | 3426 (3) | 2003 (4) |
| O(7,12) | 4415 (3) | 1492 (3) | 101 (3) |
| OGe(7,8,12) | 3295 (2) | 2629 (3) | 1744 (3) |
| O(8) | 6156 (3) | 4557 (3) | 8149 (4) |
| O(8,9) | 2150 (3) | 4694 (3) | 1803 (4) |
| O(8,12) | 3281 (3) | 3438 (3) | 110 (4) |
| O(9) | 9518 (3) | 3801 (3) | 7553 (4) |
| O(9,10) | 338 (3) | 4034 (3) | 704 (4) |
| O(10) | 9735 (3) | 2088 (3) | 8726 (4) |
| O(10,11) | 1081 (3) | 931 (3) | 88 (4) |
| O(10,12) | 1693 (3) | 2398 (3) | 9613 (4) |
| O(11) | 8023 (3) | 1330 (3) | 1204 (4) |
| O(11,12) | 2844 (3) | 595 (3) | 9712 (4) |
| O(12) | 3021 (3) | 1517 (4) | 7976 (4) |
| Na(1) | 5956 (2) | 2935 (2) | 8715 (3) |
| Na(2) | 9309 (2) | 1896 (2) | 6401 (3) |
| Na(3) | 7874 (2) | 3545 (3) | 1662 (3) |
| Na(4) | 7236 (3) | 1750 (3) | 3832 (4) |
| Aq(1) | 7600 (4) | 2742 (4) | 8908 (7) |
| Aq'(1) | 4358 (3) | 3849 (4) | 8737 (4) |

Table 1 (*cont.*)

|  | $x$ | $y$ | $z$ |
|---|---|---|---|
| Aq(1,3) | 6200 (3) | 3903 (4) | 1024 (4) |
| Aq(2) | 952 (4) | 1126 (5) | 6473 (6) |
| Aq(2,4) | 7615 (4) | 2618 (5) | 6171 (6) |
| Aq'(2,4) | 8947 (5) | 1194 (6) | 4050 (6) |
| Aq(3) | 8244 (4) | 4682 (4) | 653 (5) |
| Aq(4) | 6724 (5) | 432 (5) | 4193 (5) |
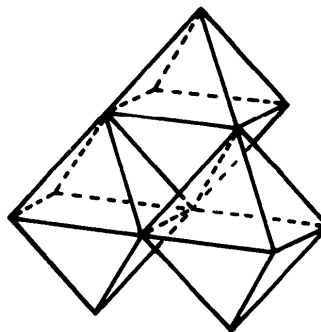


Fig. 1. A Mo$_3$O$_{13}$ group shown with idealized octahedra.
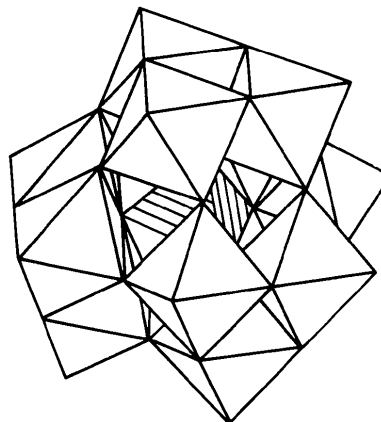


Fig. 2. The Mo$_{12}$GeO$_{40}$ group shown with idealized polyhedra.

MoO$_6$ octahedra. The twelve octahedra may be subdivided into four Mo$_3$O$_{13}$ groups (Fig. 1). In these groups each MoO$_6$ octahedron is linked to its neighbour on either side by a shared edge making one corner common to the three octahedra. The four groups are then linked to each other by sharing corners and to the GeO$_4$ tetrahedron *via* the three-coordinated O atoms. This structure is often named the Keggin molecule (Keggin, 1934). Of the five structural possibilities for 1:12 heteropolyanions suggested by Baker & Figgis (1970) this is the α isomer, which appears to be thermodynamically stable. In Fig. 2 the coupling of the twelve MoO$_6$ octahedra and the GeO$_4$ tetrahedron in the group is shown with idealized polyhedra.

Table 2. *Interatomic distances (Å) and bond angles (°) within the* $Mo_{12}GeO_{40}$ *group, with estimated standard deviations in parentheses*

Mo—Mo and Ge—Mo

| Mo(1)—Mo(3) | 3·336 (1) | Mo(5)—Mo(11) | 3·337 (1) | Ge—Mo(1) | 3·530 (1) |
|---|---|---|---|---|---|
| Mo(1)—Mo(2) | 3·381 (1) | Mo(5)—Mo(6) | 3·358 (1) | Ge—Mo(2) | 3·557 (1) |
| Mo(1)—Mo(4) | 3·732 (1) | Mo(6)—Mo(11) | 3·377 (1) | Ge—Mo(3) | 3·540 (1) |
| Mo(1)—Mo(5) | 3·741 (1) | Mo(6)—Mo(7) | 3·697 (1) | Ge—Mo(4) | 3·507 (1) |
| Mo(2)—Mo(3) | 3·337 (1) | Mo(7)—Mo(8) | 3·342 (1) | Ge—Mo(5) | 3·511 (1) |
| Mo(2)—Mo(6) | 3·715 (1) | Mo(7)—Mo(12) | 3·343 (1) | Ge—Mo(6) | 3·507 (1) |
| Mo(2)—Mo(7) | 3·743 (1) | Mo(8)—Mo(12) | 3·370 (1) | Ge—Mo(7) | 3·536 (1) |
| Mo(3)—Mo(8) | 3·731 (1) | Mo(8)—Mo(9) | 3·744 (1) | Ge—Mo(8) | 3·520 (1) |
| Mo(3)—Mo(9) | 3·779 (1) | Mo(9)—Mo(10) | 3·365 (1) | Ge—Mo(9) | 3·532 (1) |
| Mo(4)—Mo(9) | 3·317 (1) | Mo(10)—Mo(12) | 3·738 (1) | Ge—Mo(10) | 3·561 (1) |
| Mo(4)—Mo(10) | 3·346 (1) | Mo(10)—Mo(11) | 3·752 (1) | Ge—Mo(11) | 3·558 (1) |
| Mo(4)—Mo(5) | 3·737 (1) | Mo(11)—Mo(12) | 3·727 (1) | Ge—Mo(12) | 3·516 (1) |

MoO₆ octahedra

| | O(1) | O(1,5) | O(1,2) | O(1,4) | O(1,3) | OGe(1,2,3) |
|---|---|---|---|---|---|---|
| Mo(1) | 1·673 (4) | 1·812 (3) | 1·846 (3) | 2·032 (3) | 2·045 (3) | 2·289 (3) |
| O(1) | | 2·739 (5) | 2·746 (5) | 2·848 (5) | 2·776 (5) | |
| OGe(1,2,3) | | 2·895 (5) | 2·526 (5) | 2·829 (5) | 2·548 (5) | |
| O(1,5) | | | 2·778 (5) | 2·597 (5) | | |
| O(1,3) | | | 2·683 (5) | 2·658 (5) | | |
| O(1)—Mo(1)— | | 103·5 (2) | 102·5 (2) | 100·0 (2) | 96·1 (2) | |
| OGe(1,2,3)—Mo(1)— | | 89·0 (1) | 74·4 (1) | 81·6 (1) | 71·8 (1) | |
| O(1,5)—Mo(1)— | | | 98·9 (1) | 84·8 (1) | | |
| O(1,3)—Mo(1)— | | | 87·0 (1) | 81·4 (1) | | |

| | O(2) | O(2,7) | O(2,3) | O(1,2) | O(2,6) | OGe(1,2,3) |
|---|---|---|---|---|---|---|
| Mo(2) | 1·696 (4) | 1·793 (4) | 1·828 (3) | 2·045 (3) | 2·047 (3) | 2·316 (3) |
| O(2) | | 2·771 (5) | 2·743 (5) | 2·796 (5) | 2·862 (5) | |
| OGe(1,2,3) | | 2·889 (5) | 2·551 (5) | 2·526 (5) | 2·858 (4) | |
| O(2,7) | | | 2·773 (5) | | 2·591 (5) | |
| O(1,2) | | | 2·676 (5) | | 2·623 (5) | |
| O(2)—Mo(2)— | | 105·2 (2) | 102·2 (2) | 96·3 (2) | 99·4 (2) | |
| OGe(1,2,3)—Mo(2)— | | 88·4 (1) | 74·9 (1) | 70·5 (1) | 81·6 (1) | |
| O(2,7)—Mo(2)— | | | 100·0 (1) | | 84·6 (1) | |
| O(1,2)—Mo(2)— | | | 87·2 (1) | | 79·7 (1) | |

| | O(3) | O(3,9) | O(1,3) | O(2,3) | O(3,8) | OGe(1,2,3) |
|---|---|---|---|---|---|---|
| Mo(3) | 1·686 (3) | 1·821 (3) | 1·827 (3) | 2·028 (3) | 2·056 (4) | 2·284 (3) |
| O(3) | | 2·764 (5) | 2·731 (5) | 2·803 (5) | 2·839 (5) | |
| OGe(1,2,3) | | 2·833 (4) | 2·548 (5) | 2·551 (5) | 2·882 (5) | |
| O(3,9) | | | 2·781 (5) | | 2·588 (5) | |
| O(2,3) | | | 2·686 (5) | | 2·657 (5) | |
| O(3)—Mo(3)— | | 104·0 (2) | 102·0 (2) | 97·6 (2) | 98·2 (2) | |
| OGe(1,2,3)—Mo(3)— | | 86·5 (1) | 75·7 (1) | 72·3 (1) | 83·0 (1) | |
| O(3,9)—Mo(3)— | | | 99·3 (1) | | 83·5 (1) | |
| O(2,3)—Mo(3)— | | | 88·1 (1) | | 81·2 (1) | |

| | O(4) | O(1,4) | O(4,9) | O(4,5) | O(4,10) | OGe(4,9,10) |
|---|---|---|---|---|---|---|
| Mo(4) | 1·697 (4) | 1·804 (3) | 1·813 (3) | 2·038 (3) | 2·079 (4) | 2·257 (3) |
| O(4) | | 2·803 (5) | 2·751 (5) | 2·798 (5) | 2·723 (5) | |
| OGe(4,9,10) | | 2·876 (5) | 2·532 (5) | 2·815 (4) | 2·560 (4) | |
| O(1,4) | | | 2·772 (5) | 2·600 (5) | | |
| O(4,10) | | | 2·677 (5) | 2·687 (5) | | |
| O(4)—Mo(4)— | | 106·4 (2) | 103·2 (2) | 96·6 (2) | 91·7 (2) | |
| OGe(4,9,10)—Mo(4)— | | 89·4 (1) | 76·1 (1) | 81·7 (1) | 72·2 (1) | |
| O(1,4)—Mo(4)— | | | 100·1 (1) | 84·9 (1) | | |
| O(4,10)—Mo(4)— | | | 86·6 (1) | 81·4 (1) | | |

# MULTICOMPONENT POLYANIONS. 17

Table 2 (cont.)

|  | O(5) | O(4,5) | O(5,11) | O(5,6) | O(1,5) | OGe(5,6,11) |
|---|---|---|---|---|---|---|
| Mo(5) | 1·693 (4) | 1·811 (3) | 1·827 (3) | 2·034 (3) | 2·045 (3) | 2·265 (4) |
| O(5) |  | 2·759 (5) | 2·756 (5) | 2·776 (5) | 2·800 (5) |  |
| OGe(5,6,11) |  | 2·861 (5) | 2·547 (5) | 2·527 (5) | 2·854 (5) |  |
| O(4,5) |  |  | 2·762 (5) |  | 2·612 (5) |  |
| O(5,6) |  |  | 2·697 (5) |  | 2·636 (5) |  |
| O(5)—Mo(5)— |  | 103·9 (2) | 103·0 (2) | 95·9 (2) | 96·5 (2) |  |
| OGe(5,6,11)—Mo(5)— |  | 88·4 (1) | 76·2 (1) | 71·8 (1) | 82·7 (1) |  |
| O(4,5)—Mo(5)— |  |  | 98·8 (1) |  | 85·0 (1) |  |
| O(5,6)—Mo(5)— |  |  | 88·5 (1) |  | 80·5 (1) |  |

|  | O(6) | O(2,6) | O(5,6) | O(6,7) | O(6,11) | OGe(5,6,11) |
|---|---|---|---|---|---|---|
| Mo(6) | 1·683 (4) | 1·789 (3) | 1·861 (3) | 1·989 (4) | 2·084 (4) | 2·292 (3) |
| O(6) |  | 2·765 (5) | 2·762 (5) | 2·811 (6) | 2·756 (6) |  |
| OGe(5,6,11) |  | 2·912 (5) | 2·527 (5) | 2·803 (5) | 2·550 (5) |  |
| O(2,6) |  |  | 2·778 (5) | 2·595 (5) |  |  |
| O(6,11) |  |  | 2·675 (5) | 2·658 (5) |  |  |
| O(6)—Mo(6)— |  | 105·5 (2) | 102·3 (2) | 99·6 (2) | 93·4 (2) |  |
| OGe(5,6,11)—Mo(6)— |  | 90·2 (1) | 74·2 (1) | 81·5 (1) | 71·1 (1) |  |
| O(2,6)—Mo(6)— |  |  | 99·1 (1) | 86·6 (1) |  |  |
| O(6,11)—Mo(6)— |  |  | 85·2 (1) | 81·4 (1) |  |  |

|  | O(7) | O(6,7) | O(7,12) | O(7,8) | O(2,7) | OGe(7,8,12) |
|---|---|---|---|---|---|---|
| Mo(7) | 1·691 (4) | 1·807 (4) | 1·811 (4) | 2·034 (4) | 2·054 (4) | 2·299 (3) |
| O(7) |  | 2·772 (5) | 2·780 (5) | 2·784 (5) | 2·797 (5) |  |
| OGe(7,8,12) |  | 2·853 (5) | 2·545 (5) | 2·537 (5) | 2·856 (5) |  |
| O(6,7) |  |  | 2·748 (5) |  | 2·598 (5) |  |
| O(7,8) |  |  | 2·671 (5) |  | 2·646 (5) |  |
| O(7)—Mo(7)— |  | 104·8 (2) | 105·1 (2) | 96·3 (2) | 96·2 (2) |  |
| OGe(7,8,12)—Mo(7)— |  | 87·2 (1) | 75·5 (1) | 71·4 (1) | 81·8 (1) |  |
| O(6,7)—Mo(7)— |  |  | 98·9 (2) |  | 84·3 (1) |  |
| O(7,8)—Mo(7)— |  |  | 87·8 (2) |  | 80·7 (1) |  |

|  | O(8) | O(3,8) | O(7,8) | O(8,9) | O(8,12) | OGe(7,8,12) |
|---|---|---|---|---|---|---|
| Mo(8) | 1·688 (4) | 1·795 (4) | 1·842 (4) | 2·035 (4) | 2·066 (4) | 2·266 (3) |
| O(8) |  | 2·764 (6) | 2·751 (5) | 2·822 (6) | 2·748 (6) |  |
| OGe(7,8,12) |  | 2·903 (5) | 2·537 (5) | 2·818 (5) | 2·523 (5) |  |
| O(3,8) |  |  | 2·790 (5) | 2·609 (5) |  |  |
| O(8,12) |  |  | 2·710 (5) | 2·618 (5) |  |  |
| O(8)—Mo(8)— |  | 105·0 (2) | 102·3 (2) | 98·2 (2) | 93·6 (2) |  |
| OGe(7,8,12)—Mo(8)— |  | 90·5 (1) | 75·5 (1) | 81·7 (1) | 71·1 (1) |  |
| O(3,8)—Mo(8)— |  |  | 100·2 (2) | 85·7 (1) |  |  |
| O(8,12)—Mo(8)— |  |  | 87·6 (2) | 79·4 (1) |  |  |

|  | O(9) | O(8,9) | O(9,10) | O(4,9) | O(3,9) | OGe(4,9,10) |
|---|---|---|---|---|---|---|
| Mo(9) | 1·692 (4) | 1·817 (4) | 1·825 (4) | 2·038 (3) | 2·047 (3) | 2·289 (3) |
| O(9) |  | 2·773 (6) | 2·757 (5) | 2·776 (5) | 2·846 (5) |  |
| OGe(4,9,10) |  | 2·886 (5) | 2·545 (5) | 2·532 (5) | 2·823 (5) |  |
| O(8,9) |  |  | 2·787 (5) |  | 2·575 (5) |  |
| O(4,9) |  |  | 2·675 (5) |  | 2·658 (5) |  |
| O(9)—Mo(9)— |  | 104·3 (2) | 103·2 (2) | 95·7 (2) | 98·7 (2) |  |
| OGe(4,9,10)—Mo(9)— |  | 88·5 (1) | 75·5 (1) | 71·4 (1) | 81·0 (1) |  |
| O(8,9)—Mo(9)— |  |  | 99·8 (2) |  | 83·4 (1) |  |
| O(4,9)—Mo(9)— |  |  | 87·5 (1) |  | 81·2 (1) |  |

|  | O(10) | O(10,11) | O(4,10) | O(10,12) | O(9,10) | OGe(4,9,10) |
|---|---|---|---|---|---|---|
| Mo(10) | 1·697 (4) | 1·794 (4) | 1·831 (3) | 2·040 (4) | 2·074 (4) | 2·299 (3) |
| O(10) |  | 2·778 (5) | 2·752 (5) | 2·828 (5) | 2·801 (5) |  |
| OGe(4,9,10) |  | 2·873 (5) | 2·560 (4) | 2·847 (5) | 2·545 (5) |  |
| O(10,11) |  |  | 2·792 (5) | 2·595 (5) |  |  |
| O(9,10) |  |  | 2·670 (5) | 2·654 (5) |  |  |
| O(10)—Mo(10)— |  | 105·4 (2) | 102·4 (2) | 97·9 (2) | 95·4 (2) |  |
| OGe(4,9,10)—Mo(10)— |  | 88·2 (1) | 75·6 (1) | 81·7 (1) | 71·0 (1) |  |
| O(10,11)—Mo(10)— |  |  | 100·7 (2) | 85·0 (2) |  |  |
| O(9,10)—Mo(10)— |  |  | 86·0 (1) | 80·3 (1) |  |  |

Table 2 (cont.)

|  | O(11) | O(11,12) | O(6,11) | O(5,11) | O(10,11) | OGe(5,6,11) |
|---|---|---|---|---|---|---|
| Mo(11) | 1·692 (4) | 1·804 (4) | 1·823 (4) | 2·043 (3) | 2·063 (4) | 2·316 (4) |
| O(11) |  | 2·787 (5) | 2·745 (6) | 2·804 (5) | 2·872 (5) |  |
| OGe(5,6,11) |  | 2·848 (5) | 2·550 (5) | 2·547 (5) | 2·862 (5) |  |
| O(11,12) |  |  | 2·776 (5) |  | 2·587 (5) |  |
| O(5,11) |  |  | 2·670 (5) |  | 2·646 (5) |  |
| O(11)–Mo(11)– |  | 105·7 (2) | 102·6 (2) | 96·8 (2) | 99·3 (2) |  |
| OGe(5,6,11)–Mo(11)– |  | 86·5 (1) | 75·0 (1) | 71·2 (1) | 81·4 (1) |  |
| O(11,12)–Mo(11)– |  |  | 99·9 (2) |  | 83·7 (2) |  |
| O(5,11)–Mo(11)– |  |  | 87·2 (1) |  | 80·3 (1) |  |

|  | O(12) | O(10,12) | O(8,12) | O(11,12) | O(7,12) | OGe(7,8,12) |
|---|---|---|---|---|---|---|
| Mo(12) | 1·678 (4) | 1·816 (4) | 1·839 (4) | 2·013 (4) | 2·056 (4) | 2·293 (3) |
| O(12) |  | 2·739 (6) | 2·742 (6) | 2·830 (6) | 2·788 (5) |  |
| OGe(7,8,12) |  | 2·917 (5) | 2·523 (5) | 2·837 (5) | 2·545 (5) |  |
| O(10,12) |  |  | 2·765 (5) | 2·589 (5) |  |  |
| O(7,12) |  |  | 2·698 (5) | 2·657 (5) |  |  |
| O(12)–Mo(12)– |  | 103·2 (2) | 102·4 (2) | 99·7 (2) | 96·1 (2) |  |
| OGe(7,8,12)–Mo(12)– |  | 89·7 (1) | 74·4 (1) | 82·2 (1) | 71·4 (1) |  |
| O(10,12)–Mo(12)– |  |  | 98·3 (2) | 85·0 (2) |  |  |
| O(7,12)–Mo(12)– |  |  | 87·5 (1) | 81·5 (1) |  |  |

GeO$_4$ tetrahedron

|  | OGe(5,6,11) | OGe(7,8,12) | OGe(1,2,3) | OGe(4,9,10) |
|---|---|---|---|---|
| Ge | 1·724 (3) | 1·729 (3) | 1·730 (3) | 1·742 (3) |
| OGe(5,6,11) |  | 2·832 (5) | 2·822 (5) | 2·819 (4) |
| OGe(7,8,12) |  |  | 2·815 (5) | 2·829 (4) |
| OGe(1,2,3) |  |  |  | 2·846 (4) |
| OGe(5,6,11)–Ge– |  | 110·2 (2) | 109·6 (2) | 108·8 (1) |
| OGe(7,8,12)–Ge– |  |  | 108·9 (1) | 109·2 (1) |
| OGe(1,2,3)–Ge– |  |  |  | 110·1 (1) |

Distances within the group are collected in Table 2. It can be seen that when the MoO$_6$ octahedra share edges the Mo—Mo distances vary between 3·32 and 3·38 Å and when sharing corners they increase to 3·70–3·78 Å. These distances are in good agreement with those found in similar structures (Strandberg, 1975; Hedman, 1977).

## The MoO$_6$ octahedra

As can be seen from the distances and angles in Table 2, the MoO$_6$ octahedra are somewhat distorted.
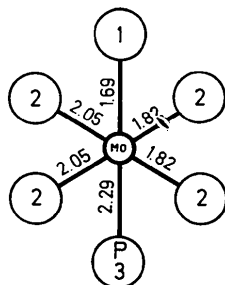


Fig. 3. A schematic figure of a MoO$_6$ octahedron. The numbers within the circles, representing O atoms, refer to the number of coordinating Mo atoms. The distances given are mean values.

The trend of increasing distances with increasing coordination numbers found in many other structures (Hedman, 1977) is also found in this investigation. Each octahedron comprises one unshared O atom, one O atom in common with three Mo and Ge, and four O atoms shared between two Mo atoms. The Mo—O distances to two-coordinated O atoms may be divided into two groups (2 + 2) with a difference of about 0·2 Å. Consequently there are four groups of Mo—O distances: (i) 1·67–1·70 Å, O atom coordinated to one Mo atom only; (ii) 1·79–1·86 Å, O atom coordinated to two Mo atoms; (iii) 1·99–2·08 Å, O atom coordinated to two Mo atoms; and (iv) 2·26–2·32 Å, O atom coordinated to Ge as well as to three Mo atoms. O atoms in group (i) are always in a trans position relative to those in group (iv), while those in group (ii) are in a trans position relative to those in group (iii). A schematic representation of this is given in Fig. 3. The differences in Mo—O distances in the octahedra are a result of varying π-bond contributions to the bonds.

## The GeO$_4$ tetrahedron

Distances and angles within the group are collected in Table 2. The Ge—O distances are 1·72–1·74 Å and the O—O distances are 2·82–2·85 Å. These distances

and the O—Ge—O angles (109–110°) agree well with values found in other compounds containing GeO$_4$ groups (Ingri & Lundgren, 1963; Nørlund Christensen, 1970) and the tetrahedron is almost regular.

### The sodium ions and water molecules

. In the structure there are four kinds of crystallographically different Na$^+$ ions: Na(1), Na(2), Na(3) and Na(4). They are all coordinated to different group O atoms, mainly those which are unshared, and in this way O—Na—O bridges between the groups are formed. Na(4) connects two groups while the remaining Na$^+$ ions form bridges between three groups. In all there are eleven Na$^+$ ions surrounding the group and they coordinate to ten of the twelve unshared O atoms as well as to three shared O atoms.

In addition to binding to group O atoms, each Na$^+$ ion is also surrounded by water O atoms. Sodium usually coordinates six O atoms in an approximately octahedral arrangement, but in this investigation Na(1) coordinates seven, and Na(4) five.

Three of the water O atoms are coordinated to two Na$^+$ ions. This strengthens the coupling between the groups in such a way that O—Na—Aq—Na—O bridges are formed. The Na—O distances are shown in Table 3.

No attempts were made to locate the H atoms, but the O—Aq and Aq—Aq distances and O—Aq—O, O—Aq—Aq and Aq—Aq—Aq angles indicate that there is a network of hydrogen bonds in the structure.

Table 3. *Sodium–oxygen distances (Å) with estimated standard deviations in parentheses*

| | | | |
|---|---|---|---|
| Na(1)—Aq(1) | 2·291 (6) | Na(3)—Aq(1,3) | 2·345 (5) |
| Na(1)—Aq(1) | 2·337 (5) | Na(3)—Aq(3) | 2·453 (6) |
| Na(1)—Aq(1,3) | 2·423 (5) | Na(3)—O(4) | 2·580 (5) |
| Na(1)—O(8) | 2·574 (5) | Na(3)—O(4,10) | 2·614 (5) |
| Na(1)—O(2) | 2·705 (5) | Na(3)—O(1,3) | 2·623 (5) |
| Na(1)—O(6) | 2·713 (5) | Na(3)—O(11) | 2·710 (5) |
| Na(1)—O(6,11) | 2·769 (5) | Na(4)—Aq(4) | 2·256 (7) |
| Na(2)—Aq(2) | 2·346 (6) | Na(4)—O(3) | 2·357 (5) |
| Na(2)—O(9) | 2·363 (5) | Na(4)—Aq'(2,4) | 2·386 (8) |
| Na(2)—O(5) | 2·380 (4) | Na(4)—O(7) | 2·411 (6) |
| Na(2)—Aq(2,4) | 2·398 (6) | Na(4)—Aq(2,4) | 2·448 (7) |
| Na(2)—Aq'(2,4) | 2·455 (7) | | |
| Na(2)—O(10) | 2·535 (5) | | |

### References

ANTTI, B.-M. (1973). *Acta Chem. Scand.* **27**, 3513–3522.

ANTTI, B.-M. (1976). *Acta Chem. Scand.* A**30**, 24–30.

BAKER, L. C. W. & FIGGIS, J. S. (1970). *J. Amer. Chem. Soc.* **92**, 3794–3797.

CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, p. 114. London: Pergamon Press.

HEDMAN, B. (1977). *Acta Cryst.* B**33**, 3083–3090.

INGRI, N. (1963). *Acta Chem. Scand.* **17**, 597–616.

INGRI, N. & LUNDGREN, G. (1963). *Acta Chem. Scand.* **17**, 617–633.

*International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 71–98, 149. Birmingham: Kynoch Press.

KEGGIN, J. F. (1934). *Proc. Roy. Soc.* A**144**, 75–100.

NØRLUND CHRISTENSEN, A. (1970). *Acta Chem. Scand.* **24**, 1287–1293.

STRANDBERG, R. (1975). *Acta Chem. Scand.* A**29**, 350–364.