

bridging carboxylate of the present system results in the less effective packing of the metals [Zn(1)–Zn(2) 5.18 Å], *via* Zn–O–C–O–Zn chains, which is comparable to the metal bridging in [Zn(*o*-eba)₂(H₂O)] Zn–Zn 4.861 Å (Natarajan *et al.*, 1974). Nevertheless, the development of a sheet-type polymeric structure in the present system, together with the presence of H-bonds between adjacent sheets, would appear to favour the use of malonic acid over *o*-eba as a fortifying agent in the ZnO/eugenol cements. In addition, the structure of [Ca(C₃H₂O₄)(H₂O)₂] (Karipides *et al.*, 1977) suggests that the adhesive interaction of malonic acid with tooth material (hydroxyapatite) yields a compound of high structural integrity which would be expected to reduce marginal leakage at the cement lute. On the other hand, the polymeric structures of [M(*o*-eba)₂(H₂O)] (M = Zn, Ca) (Natarajan *et al.*, 1974; Ray & Hathaway, 1981) are both confined to chain functions, without inter-chain H-bonds, so that cohesion is due to weak lattice-packing effects.

Subject to suitable mechanical and toxicological evaluation, the addition of malonic acid to the ZnO/eugenol cement formulations as a fortifying agent would appear to offer certain advantages over *o*-eba from a structural viewpoint; these advantages might be further enhanced through the incorporation of larger cations [*e.g.* Ca(OH)₂] in the cement powder.

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Multicomponent Polyanions.

31. The Structure of Tetraguanidinium Dodecamolybdo germanate,



BY ROLF STRANDBERG AND BRITT HEDMAN

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

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Abstract

[C(NH₂)₃]₄Mo₁₂GeO₄₀, *M_r* = 2104.3, crystallizes in the triclinic system, space group *P* $\bar{1}$, with *a* = 12.123 (2), *b* = 12.159 (2), *c* = 16.655 (3) Å, α = 76.35 (1), β = 78.46 (1), γ = 66.99 (1)°, *V* = 2180 Å³ and *Z* = 2 [this is the reduced cell; Donnay's conventional reduced cell may be obtained by applying the transformation (0 $\bar{1}$ 0/001/100)]; *D_x* = 3.21 Mg

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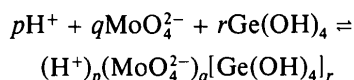
m⁻³, $\mu(\text{Mo } K\alpha) = 4.10 \text{ mm}^{-1}$. The final *R* = 0.050, based on 5471 independent reflexions. The structure contains Mo₁₂GeO₄₀⁴⁻ anions joined in a three-dimensional framework by hydrogen and ionic bonds from the [C(NH₂)₃]⁺ cations. The heteropolyanion has the well-known Keggin structure (*α* isomer). Mean Mo–Mo distances are 3.35 Å for edge-sharing MoO₆ octahedra and 3.73 Å when a corner is shared. The Mo–O distances are distributed in three different

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groups, depending on coordination, with mean values of 1.69, 1.93 and 2.29 Å. The GeO_4 tetrahedron is almost regular and the Ge—O distances vary between 1.729 and 1.745 Å. The guanidinium ions are approximately planar with a mean C—N distance of 1.33 Å.

Introduction

The present crystal structure forms part of a research project in this department aimed at elucidating the equilibria and structures of three-component complexes present in aqueous solution. One of the systems studied contains the reacting components H^+ , MoO_4^{2-} and $\text{Ge}(\text{OH})_4$ and the equilibria may be written



where p , q and r are integers defining the complexes formed. The equilibrium analyses, using potentiometric and spectrophotometric methods (298 K, 3.0 M NaClO_4 medium), indicate the presence of complexes with $q:r$ ratios of 6:1, 9:1 and 12:1 (Pettersson, 1981).

To obtain structural information on the complexes formed, X-ray diffraction investigations of crystalline phases, obtained from titration solutions as well as from crystallization experiments, are performed. Both inorganic and organic cations have been used to obtain the crystalline phases.

This paper reports a structure investigation of a complex which, in (p,q,r) notation, should be written (20,12,1).

Experimental

Crystal preparation and data

For the crystallization experiments 8.0 g of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ and 0.39 g of GeO_2 were dissolved in 100 ml 0.51 M HClO_4 solution. [The dissolution of GeO_2 was carried out according to Ingri (1963).] 0.021 g of $\text{C}(\text{NH}_2)_3\text{Cl}$ was added to 7.5 ml of the solution which then was set for evaporation at room temperature. Within a few days light-yellow prismatic crystals were obtained. To prevent decomposition, the crystal was sealed in a glass capillary during the X-ray investigation. A test in bromoform showed that the crystals have a density greater than 2.89 Mg m^{-3} . Weissenberg photographs indicated triclinic symmetry, and the space group $P\bar{1}$ was established in the structure determination. Cell parameters were obtained by least-squares refinement from 25 reflexions ($27^\circ < 2\theta < 43^\circ$) automatically centred on a Syntex R3 four-circle diffractometer.

Table 1. Fractional atomic coordinates ($\times 10^4$; for Mo and Ge $\times 10^5$) and B_{eq} (Hamilton, 1959)

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.

	x	y	z	B_{eq} (Å ²)
Mo(1)	57160 (10)	-7936 (10)	24659 (9)	1.56 (4)
Mo(2)	4442 (11)	16047 (12)	38671 (9)	1.89 (4)
Mo(3)	29501 (11)	44191 (11)	31097 (9)	1.64 (4)
Mo(4)	54635 (11)	19426 (11)	32469 (9)	1.75 (4)
Mo(5)	34239 (12)	-8832 (11)	39564 (8)	1.69 (4)
Mo(6)	29879 (13)	20046 (12)	45835 (8)	1.99 (4)
Mo(7)	2339 (10)	42141 (10)	25386 (9)	1.66 (4)
Mo(8)	54427 (11)	21191 (12)	9822 (9)	1.92 (4)
Mo(9)	32669 (11)	-9951 (10)	19853 (8)	1.56 (4)
Mo(10)	4182 (11)	17706 (11)	18315 (9)	1.75 (4)
Mo(11)	27713 (12)	43784 (11)	8882 (9)	1.91 (4)
Mo(12)	32006 (12)	17294 (12)	3643 (8)	1.90 (4)
Ge	30217 (12)	18005 (12)	24783 (10)	0.94 (3)
O(1)	7184 (8)	-1737 (9)	2436 (7)	1.96 (32)
O(1,4)	5775 (8)	397 (8)	3087 (6)	1.41 (28)
O(1,5)	5104 (8)	-1536 (8)	3540 (6)	1.56 (29)
O(1,8)	5767 (8)	439 (8)	1545 (6)	1.66 (30)
O(1,9)	5058 (8)	-1540 (8)	1946 (6)	1.38 (29)
OGe(1,5,9)	3685 (8)	221 (7)	2653 (6)	1.10 (26)
O(2)	-515 (9)	1332 (10)	4683 (7)	2.75 (38)
O(2,5)	1739 (8)	70 (8)	3889 (6)	1.53 (30)
O(2,6)	1490 (9)	2062 (9)	4366 (6)	1.96 (33)
O(2,7)	-402 (8)	3348 (8)	3531 (6)	1.39 (28)
O(2,10)	-180 (8)	1299 (8)	2999 (6)	1.59 (30)
OGe(2,7,10)	1454 (7)	2229 (7)	2621 (6)	1.11 (26)
O(3)	2579 (9)	5856 (9)	3276 (7)	2.26 (34)
O(3,4)	4585 (8)	3753 (8)	3235 (6)	1.49 (29)
O(3,6)	2629 (8)	3659 (9)	4300 (6)	1.82 (32)
O(3,7)	1234 (8)	4484 (8)	3081 (6)	1.68 (30)
O(3,11)	3103 (8)	4554 (8)	2000 (6)	1.70 (30)
OGe(3,4,6)	3470 (7)	2386 (8)	3159 (5)	1.14 (27)
O(4)	6847 (8)	1881 (9)	3375 (7)	2.33 (35)
O(4,6)	4725 (8)	1755 (8)	4349 (6)	1.53 (30)
O(4,8)	5572 (8)	2394 (8)	2028 (6)	1.63 (30)
O(5)	3374 (9)	-2002 (9)	4754 (6)	2.07 (33)
O(5,6)	3538 (8)	286 (8)	4404 (6)	1.72 (31)
O(5,9)	3217 (8)	-1703 (8)	3067 (6)	1.57 (29)
O(6)	2843 (10)	1788 (11)	5626 (6)	2.59 (39)
O(7)	-940 (8)	5536 (9)	2450 (7)	2.30 (33)
O(7,10)	-415 (8)	3380 (8)	1907 (6)	1.81 (31)
O(7,11)	1251 (7)	4431 (8)	1525 (6)	1.46 (28)
O(8)	6811 (9)	2025 (10)	470 (7)	2.68 (38)
O(8,11)	4522 (8)	3805 (8)	657 (6)	1.76 (30)
O(8,12)	4772 (8)	1769 (8)	129 (6)	1.60 (30)
OGe(8,11,12)	3471 (7)	2356 (7)	1463 (5)	1.01 (25)
O(9)	3248 (8)	-2071 (8)	1499 (7)	2.13 (33)
O(9,10)	1708 (8)	95 (8)	1999 (6)	1.52 (29)
O(9,12)	3582 (8)	221 (8)	965 (6)	1.63 (29)
O(10)	-510 (9)	1438 (9)	1369 (7)	2.31 (36)
O(10,12)	1526 (8)	2086 (8)	948 (6)	1.66 (31)
O(11)	2393 (10)	5860 (9)	406 (7)	2.67 (36)
O(11,12)	2643 (8)	3621 (9)	127 (6)	1.90 (32)
O(12)	2951 (9)	1585 (10)	-552 (6)	2.36 (37)
C(1)	6372 (12)	5193 (13)	1596 (10)	1.99 (46)
C(2)	6243 (15)	5208 (14)	3960 (12)	3.22 (60)
C(3)	-325 (12)	-1644 (13)	3276 (10)	2.05 (45)
C(4)	-184 (15)	-1477 (16)	889 (11)	2.90 (58)
N(11)	7105 (12)	4045 (12)	1630 (11)	3.66 (55)
N(12)	6681 (12)	5996 (12)	1821 (8)	2.59 (45)
N(13)	5277 (12)	5525 (12)	1349 (10)	3.11 (49)
N(21)	6974 (14)	4076 (13)	3959 (13)	4.79 (65)
N(22)	6681 (14)	6009 (13)	4069 (11)	3.81 (59)
N(23)	5132 (13)	5567 (15)	3820 (13)	4.79 (68)
N(31)	-460 (12)	-2632 (12)	3193 (11)	3.43 (53)
N(32)	692 (11)	-1694 (12)	3453 (10)	2.74 (46)
N(33)	-1234 (11)	-583 (11)	3214 (10)	2.84 (46)
N(41)	-219 (13)	-2481 (14)	726 (11)	4.26 (62)
N(42)	891 (14)	-1357 (17)	923 (12)	4.92 (71)
N(43)	-1208 (11)	-541 (12)	1011 (10)	3.08 (49)

Table 2 (cont.)

O(9)—Mo(9)—O(1.9)	97.4 (5)	OGe(1.5,9)—Mo(9)—O(9.10)	88.1 (4)
O(9)—Mo(9)—O(5.9)	102.9 (5)	OGe(1.5,9)—Mo(9)—O(9.12)	81.3 (4)
O(9)—Mo(9)—O(9.10)	103.1 (5)	O(1.9)—Mo(9)—O(5.9)	88.4 (4)
O(9)—Mo(9)—O(9.12)	99.7 (5)	O(1.9)—Mo(9)—O(9.12)	81.4 (4)
OGe(1.5,9)—Mo(9)—O(1.9)	71.6 (4)	O(9.10)—Mo(9)—O(5.9)	98.7 (4)
OGe(1.5,9)—Mo(9)—O(5.9)	75.1 (4)	O(9.10)—Mo(9)—O(9.12)	83.5 (4)
Mo(10)—O(10)	1.696 (12)	O(10)—O(10,12)	2.788 (16)
Mo(10)—O(2,10)	1.967 (10)	OGe(2.7,10)—O(2,10)	2.552 (14)
Mo(10)—O(7,10)	1.840 (10)	OGe(2.7,10)—O(7,10)	2.513 (14)
Mo(10)—O(9,10)	2.022 (9)	OGe(2.7,10)—O(9,10)	2.900 (13)
Mo(10)—O(10,12)	1.860 (10)	OGe(2.7,10)—O(10,12)	2.813 (13)
Mo(10)—OGe(2.7,10)	2.273 (10)	O(2,10)—O(7,10)	2.695 (14)
O(10)—O(2,10)	2.780 (15)	O(2,10)—O(9,10)	2.675 (14)
O(10)—O(7,10)	2.765 (15)	O(10,12)—O(7,10)	2.711 (14)
O(10)—O(9,10)	2.809 (15)	O(10,12)—O(9,10)	2.590 (13)
O(10)—Mo(10)—O(2,10)	98.5 (5)	OGe(2.7,10)—Mo(10)—O(9,10)	84.7 (4)
O(10)—Mo(10)—O(7,10)	102.8 (5)	OGe(2.7,10)—Mo(10)—O(10,12)	85.2 (4)
O(10)—Mo(10)—O(9,10)	97.7 (5)	O(2,10)—Mo(10)—O(7,10)	90.1 (4)
O(10)—Mo(10)—O(10,12)	103.2 (5)	O(2,10)—Mo(10)—O(9,10)	84.2 (4)
OGe(2.7,10)—Mo(10)—O(2,10)	73.6 (4)	O(10,12)—Mo(10)—O(7,10)	94.2 (4)
OGe(2.7,10)—Mo(10)—O(7,10)	74.5 (4)	O(10,12)—Mo(10)—O(9,10)	83.6 (4)
Mo(11)—O(11)	1.709 (10)	O(11)—O(11,12)	2.760 (14)
Mo(11)—O(3,11)	2.047 (10)	OGe(8,11,12)—O(3,11)	2.860 (13)
Mo(11)—O(7,11)	1.919 (10)	OGe(8,11,12)—O(7,11)	2.885 (13)
Mo(11)—O(8,11)	1.945 (11)	OGe(8,11,12)—O(8,11)	2.547 (14)
Mo(11)—O(11,12)	1.794 (10)	OGe(8,11,12)—O(11,12)	2.529 (14)
Mo(11)—OGe(8,11,12)	2.295 (9)	O(3,11)—O(7,11)	2.592 (15)
O(11)—O(3,11)	2.858 (15)	O(3,11)—O(8,11)	2.644 (14)
O(11)—O(7,11)	2.780 (15)	O(11,12)—O(7,11)	2.729 (14)
O(11)—O(8,11)	2.825 (15)	O(11,12)—O(8,11)	2.705 (16)
O(11)—Mo(11)—O(3,11)	98.7 (5)	OGe(8,11,12)—Mo(11)—O(8,11)	73.3 (4)
O(11)—Mo(11)—O(7,11)	99.9 (5)	OGe(8,11,12)—Mo(11)—O(11,12)	75.3 (4)
O(11)—Mo(11)—O(8,11)	101.1 (5)	O(3,11)—Mo(11)—O(7,11)	81.5 (4)
O(11)—Mo(11)—O(11,12)	103.9 (5)	O(3,11)—Mo(11)—O(8,11)	82.9 (4)
OGe(8,11,12)—Mo(11)—O(3,11)	82.2 (4)	O(11,12)—Mo(11)—O(7,11)	94.5 (4)
OGe(8,11,12)—Mo(11)—O(7,11)	85.9 (4)	O(11,12)—Mo(11)—O(8,11)	92.6 (4)
Mo(12)—O(12)	1.674 (11)	O(12)—O(11,12)	2.824 (15)
Mo(12)—O(8,12)	1.885 (11)	OGe(8,11,12)—O(8,12)	2.530 (13)
Mo(12)—O(9,12)	1.799 (10)	OGe(8,11,12)—O(9,12)	2.854 (13)
Mo(12)—O(10,12)	1.994 (11)	OGe(8,11,12)—O(10,12)	2.820 (15)
Mo(12)—O(11,12)	2.089 (10)	OGe(8,11,12)—O(11,12)	2.529 (14)
Mo(12)—OGe(8,11,12)	2.266 (9)	O(8,12)—O(9,12)	2.766 (14)
O(12)—O(8,12)	2.779 (16)	O(8,12)—O(11,12)	2.681 (15)
O(12)—O(9,12)	2.743 (15)	O(10,12)—O(9,12)	2.634 (14)
O(12)—O(10,12)	2.787 (15)	O(10,12)—O(11,12)	2.686 (15)
O(12)—Mo(12)—O(8,12)	102.5 (5)	OGe(8,11,12)—Mo(12)—O(10,12)	82.6 (4)
O(12)—Mo(12)—O(9,12)	104.3 (5)	OGe(8,11,12)—Mo(12)—O(11,12)	70.9 (4)
O(12)—Mo(12)—O(10,12)	98.5 (5)	O(8,12)—Mo(12)—O(9,12)	97.3 (4)
O(12)—Mo(12)—O(11,12)	96.6 (5)	O(8,12)—Mo(12)—O(11,12)	84.7 (4)
OGe(8,11,12)—Mo(12)—O(8,12)	74.5 (4)	O(10,12)—Mo(12)—O(9,12)	87.8 (4)
OGe(8,11,12)—Mo(12)—O(9,12)	88.4 (4)	O(10,12)—Mo(12)—O(11,12)	82.2 (4)
Ge—OGe(1.5,9)	1.744 (8)	OGe(1.5,9)—OGe(3,4,6)	2.852 (13)
Ge—OGe(2.7,10)	1.745 (10)	OGe(1.5,9)—OGe(8,11,12)	2.824 (12)
Ge—OGe(3,4,6)	1.738 (9)	OGe(2.7,10)—OGe(3,4,6)	2.854 (14)
Ge—OGe(8,11,12)	1.729 (9)	OGe(2.7,10)—OGe(8,11,12)	2.827 (13)
OGe(1.5,9)—OGe(2.7,10)	2.849 (13)	OGe(3,4,6)—OGe(8,11,12)	2.833 (13)
OGe(1.5,9)—Ge—OGe(2.7,10)	109.5 (4)	OGe(2.7,10)—Ge—OGe(3,4,6)	110.0 (4)
OGe(1.5,9)—Ge—OGe(3,4,6)	110.0 (4)	OGe(2.7,10)—Ge—OGe(8,11,12)	108.9 (4)
OGe(1.5,9)—Ge—OGe(8,11,12)	108.8 (4)	OGe(3,4,6)—Ge—OGe(8,11,12)	109.6 (4)

Structure determination and refinement

The centrosymmetric space group $P\bar{1}$ was chosen and the structure determination could be successfully completed in this. From a Patterson synthesis the Ge and Mo atoms were located and routine heavy-atom methods yielded the positions of the anion O and non-hydrogen atoms of the $[C(NH_2)_3]^+$ cations. Block-diagonal least-squares refinement, with anisotropic thermal parameters, converged at $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.050$ and $R_w = [\sum w_i (|F_o| - |F_c|)^2 / \sum w_i |F_o|^2]^{1/2} = 0.056$.

A weighting scheme, $w = 1/\sigma^2(F_o)$, was applied in which $\sigma^2(F_o)$ was modified to $\sigma^2(F_o) = \sigma_o^2(F_o) + (0.015F_o)^2$. In the final cycle, the parameter shifts were $<0.1\sigma$. Mo³⁺, Ge, O⁻, C and N scattering factors were used and account was taken of the real and imaginary parts of the anomalous dispersion (*International*

Tables for X-ray Crystallography, 1974). The final difference synthesis showed no anomalies.

The computer programs were those supplied with the Syntex R3 crystallographic system, and the computations were made on a Data General Nova 3 computer. Final atomic positional parameters are given in Table 1.*

Description and discussion of the structure

The structure consists of $Mo_{12}GeO_{40}^{4-}$ anions joined in a three-dimensional framework by numerous hydrogen bonds to the $C(NH_2)_3^+$ cations.

The $Mo_{12}GeO_{40}^{4-}$ anion

This anion shows the well-known Keggin (1934) structure. In broad outline the anion consists of a central GeO_4 tetrahedron whose O atoms are part of the cage of the surrounding twelve MoO_6 octahedra. These octahedra are linked to each other by sharing corners and edges. In each octahedron only one O atom is unshared. A stereoscopic view of the anion is shown in Fig. 1.

Distances within the anion are given in Table 2. Two groups of Mo—Mo distances can be distinguished. When the MoO_6 octahedra share edges the Mo—Mo distances vary between 3.32 and 3.36 Å while when sharing corners they increase to 3.70–3.76 Å. These distances, as well as the Mo—Ge distances (3.50–3.57 Å), are in good agreement with those found in earlier investigations (e.g. Strandberg, 1977). Cross-distances, Mo—Mo, within the anion vary between 4.78 and 7.11 Å.

The MoO_6 octahedra are far from regular which can be seen from Table 2. As expected the Mo—O distances increase with the number of Mo atoms coordinating the

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36423 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

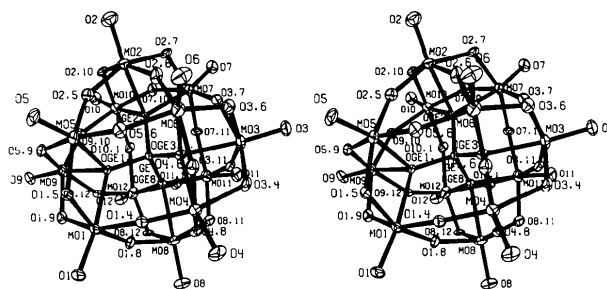


Fig. 1. A stereoscopic view of the $Mo_{12}GeO_{40}^{4-}$ anion. The thermal ellipsoids are scaled to include 50% probability.

O atom. 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. Consequently there are three groups of Mo—O distances and, according to the above, the distances within each group are: 1.66–1.71, 1.79–2.09, 2.26–2.31 Å.

The GeO_4 group is almost regular. Distances Ge—O (1.729–1.745 Å), O—O (2.825–2.853 Å) as well as angles O—Ge—O (108.8–110.0°) are in good agreement with values found in earlier investigations (Ingri & Lundgren, 1963; Nørlund Christensen, 1970; Strandberg, 1977).

The guanidinium ions

There are four crystallographically different $\text{C}(\text{NH}_2)_3^+$ ions in the structure. Although no attempts were made to locate the H atoms, structural considerations show that the ions are all taking part in hydrogen bonding between the heteropolyanions (see below).

The C and N atoms in each guanidinium ion are almost planar with C triangularly coordinated by nitrogen. The mean C—N distance is 1.33 Å while the mean value for the angle N—C—N is 120.0° (Table 3). These are in accordance with earlier results (Haas, Harris & Mills, 1965).

Hydrogen bonds

The only connecting links between the $\text{Mo}_{12}\text{GeO}_{40}^{4-}$ anions are hydrogen bonds effected by the guanidinium ions. The H atoms were not definitely located but by taking N—O distances as well as O—N—O angles into consideration, a proposal for the hydrogen-bond system can be given. The system is rather complicated and only the most obvious and strong connexions have been included.

For the sake of simplicity we can denote the four guanidinium ions $G1\dots G4$ (the numbering in accordance with C). Of these, $G1$ seems to be the most important ion. It connects anions, by hydrogen bonds $\text{O}\dots\text{H}-\text{N}-\text{H}\dots\text{O}$, in three directions [100], [010]

Table 3. Distances (Å) and angles (°) in the $[\text{C}(\text{NH}_2)_3]^+$ cations

C(1)—N(11)	1.33 (2)	N(11)—C(1)—N(12)	121 (2)
—N(12)	1.32 (2)	N(11)—C(1)—N(13)	118 (2)
—N(13)	1.35 (2)	N(12)—C(1)—N(13)	120 (1)
C(2)—N(21)	1.31 (2)	N(21)—C(2)—N(22)	119 (2)
—N(22)	1.34 (2)	N(21)—C(2)—N(23)	121 (2)
—N(23)	1.30 (3)	N(22)—C(2)—N(23)	120 (2)
C(3)—N(31)	1.32 (2)	N(31)—C(3)—N(32)	121 (2)
—N(32)	1.30 (2)	N(31)—C(3)—N(33)	121 (2)
—N(33)	1.33 (2)	N(32)—C(3)—N(33)	118 (1)
C(4)—N(41)	1.33 (2)	N(41)—C(4)—N(42)	122 (2)
—N(42)	1.38 (3)	N(41)—C(4)—N(43)	120 (2)
—N(43)	1.33 (2)	N(42)—C(4)—N(43)	118 (2)

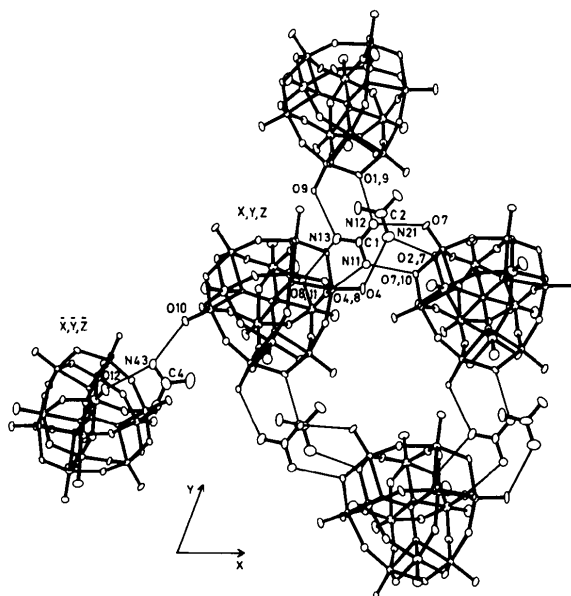


Fig. 2. Some possible hydrogen bonds, effected by the guanidinium ions, between $\text{Mo}_{12}\text{GeO}_{40}^{4-}$ anions.

Table 4. Hydrogen-bond distances (Å) and angles (°)

N(11)—O(7,10)	2.90 (2)	127.9 (6)
—O(4,8)	3.12 (2)	
N(12)—O(1,9)	2.90 (2)	109.1 (5)
—O(7)	3.07 (2)	
N(13)—O(9)	3.02 (2)	112.5 (5)
—O(8,11)	3.10 (2)	
N(21)—O(2,7)	2.93 (2)	94.0 (6)
—O(4)	3.11 (2)	
N(43)—O(10)	3.05 (2)	155.1 (6)
—O(12)	3.14 (2)	

and $[1\bar{1}0]$. All N—O distances fall into the range 2.90–3.12 Å with the angles O—N—O varying between 109 and 128° (Fig. 2). There is only one hydrogen bond of the above outlined type involving $G2$. It includes N(21) and connects anions in the [100] direction. $G3$ has no 'pure' bridge of this type but $G4$ constitutes a link between symmetry-related anions through N(43).

Apart from the pure $\text{O}\dots\text{H}-\text{N}-\text{H}\dots\text{O}$ bonds there are of course also numerous connexions of the type $\text{O}\dots\text{H}-\text{N}-\text{C}-\text{N}-\text{H}\dots\text{O}$. Moreover, many hydrogen bonds are bifurcated. Hydrogen-bond distances and angles are collected in Table 4.

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The Structures of the Monoclinic and Orthorhombic Forms of Hen Egg-White Lysozyme at 6 Å Resolution

BY P. J. ARTYMIUK, C. C. F. BLAKE, D. W. RICE* AND K. S. WILSON†

Laboratory of Molecular Biophysics, Department of Zoology, South Parks Road, Oxford OX1 3PS, England

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Abstract

The structures of a monoclinic and an orthorhombic form of hen egg-white lysozyme (HEWL) have been determined at 6 Å resolution by the method of isomorphous replacement. At this resolution the conformations of the molecules are indistinguishable from that of the tetragonal form of HEWL. The two molecules in the asymmetric unit of the monoclinic form are related by a translation of approximately $(a/2 + c/2)$. The tight packing of the molecules in the unit cell prevents substrate-binding studies being carried out on this crystal form. In the orthorhombic crystals the sugar-binding sites *A* and *B* are blocked but the lower part of the active-site cleft appears to be accessible. Thus, neither of these crystal forms is ideally suited to the binding of true substrate at sub-zero temperatures.

Crystallographic studies of the structure of the tetragonal crystal form of hen egg-white lysozyme (Blake, Mair, North, Phillips & Sarma, 1967) and its complexes with mono-, tri- and tetrasaccharides (Blake, Johnson, Mair, North, Phillips & Sarma, 1967; Ford, Johnson, Machin, Phillips & Tjian, 1974) have made a significant contribution to the understanding of enzyme activity (Phillips, 1966; Imoto, Johnson, North, Phillips & Rupley, 1972; Blake *et al.*, 1978). It now seems probable that further understanding can best be achieved by the examination of true substrate com-

plexes of the enzyme stabilized at sub-zero temperatures (Douzou, 1977; Fink & Ahmed, 1976; Alber, Tsernoglou & Petsko, 1976). For success with this technique, the active site of the crystalline enzyme must be fully accessible to allow the diffused substrate to interact to form the enzyme–substrate complex. This condition is not met in the tetragonal form, where the lower half of the active site is occluded by a neighbouring molecule (Blake *et al.*, 1967). The active site of the triclinic form of the enzyme appears to be even less accessible (Kurachi, Sieker & Jensen, 1976). To determine whether any of the known crystal forms of hen egg-white lysozyme are suitable for the low-temperature experiments, we have carried out low-resolution X-ray analyses of a monoclinic and an orthorhombic crystal form.

Materials and methods

Crystallization

Monoclinic crystals of hen egg-white lysozyme (HEWL) were grown by a slight modification of the methods reported by Crick (1953) and Steinrauf (1959). Lysozyme (Sigma Chemical Co.) was slowly dissolved in water previously adjusted to pH 4.5 by HNO₃ to a concentration of 0.5% (*w/v*). After complete dissolution of the protein the solution was brought to 3% NaNO₃ and allowed to stand in glass vials. The crystals grew in the form of large rectangular plates. To obtain the orthorhombic crystals, HEWL was made up to a 3% (*w/v*) solution in water previously adjusted to pH 9.6 by NaOH, and then brought to 2% in NaCl. Large rod-shaped crystals

* Present address: Department of Biochemistry, Sheffield University, Sheffield, England.

† Present address: Max-Planck-Institut für Molekular Genetik, Abteilung Wittmann, 63–73 Ihnestrasse, Dahlem, 33 Berlin 1000, West Germany