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$Na_{10}(glycine)_2[H_2W_{12}O_{42}]\cdot 28H_2O$

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The title compound, decasodium diglycine dihydrogenododecatetracontadodecatungstate(10−) octacosahydrate, consists of a centrosymmetric paratungstate $[H_2W_{12}O_{42}]^{10-}$ anion, ten Na^+ cations, two zwitterionic glycine molecules and 28 water molecules of crystallization. Two glycine carboxylate O atoms coordinate three different Na^+ cations, while the amino N atom forms hydrogen bonds with the paratungstate anion through both terminal and bridging O atoms.

Comment

The recent discovery of biological activities of polyoxometallates (Yamase *et al.*, 1988; Yamase, 1994) led us to focus on the interaction behaviour of polyoxometallates with biomolecules. With regard to the complexation of polyoxomolybdates with amino acids or peptides, $Na_2[Mo_8O_{26}(lysineH_2)_2]\cdot 8H_2O$ (Inoue & Yamase, 1995) and $[Mo_4O_{12}(glycylglycylglycine)_2]\cdot 9H_2O$ (Yamase *et al.*, 1999) have been obtained from aqueous molybdate solutions (pH 3) containing lysine and glycylglycylglycine, respectively. The former consists of a γ-type octamolybdate coordinated by two lysine ligands through their carboxylate O atoms. The latter consists of a polymeric $[Mo_4O_{12}]_\infty$ chain attached by glycylglycylglycine ligands through both carboxylate O atoms. As an extension of our investigation on the polyoxomolybdate-based complexes to polyoxotungstate-based ones, we recently prepared the title compound, (I), from aqueous tungstate solution in the presence of glycine at pH 7.1.

Fig. 1 shows an *ORTEP*II (Johnson, 1976) drawing of the $[H_2W_{12}O_{42}]^{10-}$ anion, which is isostructural with those of known paratungstate salts, for instance, $Na_{10}[H_2W_{12}O_{42}]\cdot 20H_2O$ (Evans & Rollins, 1976) and $Na_{10}[H_2W_{12}O_{42}]\cdot 26H_2O$ (Cruywagen *et al.*, 1986). The two protons in the centrosymmetric $[H_2W_{12}O_{42}]^{10-}$ anion are attached to triply bridging O5 and O5^i atoms, as shown by their low bond valence sum (1.09; Brown, 1980). The W—O distances and O—W—O angles are essentially similar to those of other paratungstate compounds.

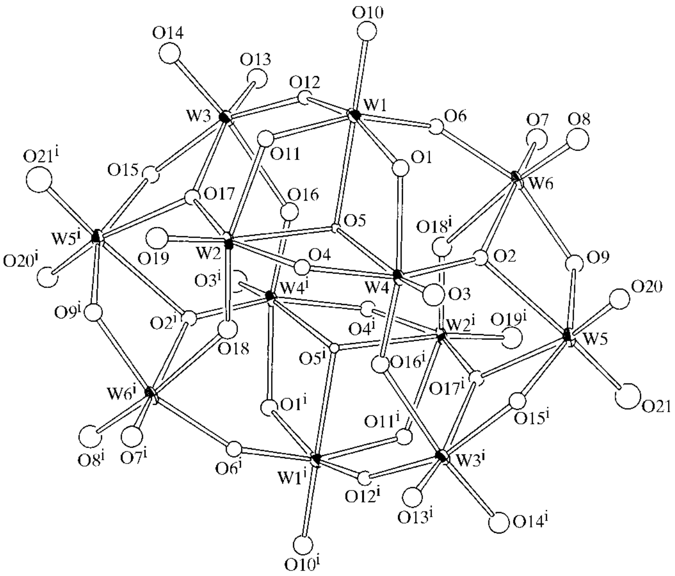

Figure 1
*ORTEP*II (Johnson, 1976) plot of the $[H_2W_{12}O_{42}]^{10-}$ anion [symmetry code: (i) $-x, -y, -1-z$]. Displacement ellipsoids are drawn at the 50% probabilty level.

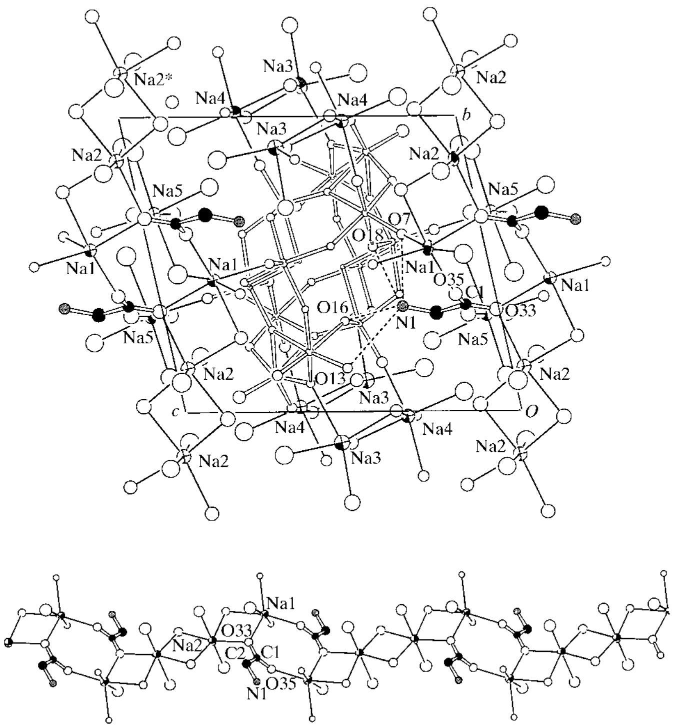

Figure 2
*ORTEP*II (Johnson, 1976) drawings of the unit-cell packing viewed parallel to the *a* axis (top) and the $[(glycine)_2Na_4O_{14}]_\infty$ chain (bottom). Na···O and N···O hydrogen bonds are denoted by thin solid and broken lines, respectively. C and N atoms of glycine are represented by filled and shaded circles, respectively. Displacement ellipsoids are drawn at the 50% probability level.

Since the negative charge of the $[H_2W_{12}O_{42}]^{10-}$ anion is completely compensated by Na^+ cations, the glycine molecule seems to be zwitterionic. Fig. 2 (top) is a packing diagram of (I). Each of the Na^+ cations is octahedrally coordinated by six O atoms belonging to $[H_2W_{12}O_{42}]^{10-}$ anions, crystallization water molecules or carboxylate O atoms (Table 1). As shown in Fig. 2 (bottom), four NaO_6 octahedra, including Na1, Na2 and their symmetry-related Na atoms, are linearly connected by edge-sharing and linked by the glycine molecules through carboxylate O33 and O35 atoms [with distances of Na1—O33 2.41 (1), Na1—O35 2.37 (1) and Na2—O33 2.46 (1) Å] to form a polymeric $[(\text{glycine})_2\text{Na}_4\text{O}_{14}]_\infty$ chain running along the *b* axis. Furthermore, as shown in Fig. 2 (top), the amino N1 of the glycine is hydrogen bonded to a neighbouring $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$ anion at its terminal (O7, O13) and bridging (O16, O18) atoms, with N···O distances of 2.85 (2), 3.16 (2), 3.04 (2) and 2.98 (2) Å, respectively (Table 2).

In conclusion, unlike the polyoxomolybdate–amino acid complexes, in the title compound the glycine molecule interacts with the paratungstate anion by N···O hydrogen bonding without any direct coordination of the carboxylate O atoms to the W centre.

Experimental

An aqueous solution containing $\text{Na}_2\text{WO}_4\cdot2\text{H}_2\text{O}$ (12.0 g) and glycine (1.0 g) was stirred for 10 min at pH 10. H_3PO_4 (85%, 0.28 ml) was added and the solution stirred for another 15 min at pH 9. A slow dropwise addition of HCl (12 *M*, 3.5 ml) to the solution with stirring gradually led to the formation of a white precipitate. The solution was filtered after stirring for 4 h. Colourless single crystals of (I) were obtained from the filtrate (at pH 7.1) after a few days.

Crystal data

$\text{Na}_{10}[\text{H}_2\text{W}_{12}\text{O}_{42}]\cdot2\text{C}_2\text{H}_5\text{NO}_2\cdot28\text{H}_2\text{O}$
$M_r = 3764.65$
Triclinic, $P\bar{1}$
$a = 11.86$ (1) Å
$b = 12.60$ (1) Å
$c = 13.02$ (2) Å
$\alpha = 74.3$ (1)°
$\beta = 79.6$ (1)°
$\gamma = 66.0$ (1)°
$V = 1706$ (8) Å^3

$Z = 1$
$D_x = 3.664$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.0$–12.5°
$\mu = 20.356$ mm^{-1}
$T = 298$ K
Plate, colourless
0.12 × 0.12 × 0.05 mm

Data collection

Rigaku AFC-5*S* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.108$, $T_{\max} = 0.369$
8194 measured reflections
7818 independent reflections
7188 reflections with $F^2 > \sigma(F^2)$

$R_{\text{int}} = 0.055$
$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 15$
$k = -14 \rightarrow 16$
$k = -16 \rightarrow 16$
3 standard reflections every 100 reflections intensity decay: 5.90%

Refinement

Refinement on F
$R[F^2 > \sigma(F^2)] = 0.051$
$wR(F) = 0.063$
$S = 1.980$
7188 reflections
260 parameters

H-atom parameters not defined
$w = 1/[\sigma^2(F_o) + 0.00036|F_o|^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 3.86$ e Å^{-3}
$\Delta\rho_{\max} = -4.63$ e Å^{-3}

Since the large positive (3.86 e Å^{-3}) and negative (−4.63 e Å^{-3}) difference Fourier peaks are located at short distances from W2 (1.04 Å) and W6 (0.90 Å), respectively, these peaks can be attributed to ghosts of the heavy W atoms.

Table 1
Selected geometric parameters (Å).

Na1—O7	2.35 (1)	Na3—O28	2.39 (1)
Na1—O35	2.37 (1)	Na3—O13$^{\text{v}}$	2.62 (1)
Na1—O33$^{\text{i}}$	2.41 (1)	Na3—O15$^{\text{vi}}$	2.63 (1)
Na1—O10$^{\text{ii}}$	2.44 (1)	Na4—O3	2.28 (1)
Na1—O34	2.49 (1)	Na4—O8$^{\text{vii}}$	2.35 (1)
Na1—O25$^{\text{iii}}$	3.10 (2)	Na4—O30	2.35 (2)
Na2—O32	2.30 (1)	Na4—O28	2.36 (1)
Na2—O34	2.33 (1)	Na4—O29	2.45 (1)
Na2—O31	2.44 (2)	Na4—O20$^{\text{vii}}$	2.46 (1)
Na2—O33$^{\text{i}}$	2.46 (1)	Na5—O24	2.38 (1)
Na2—O32$^{\text{iv}}$	2.50 (1)	Na5—O23	2.38 (1)
Na2—O36	2.52 (2)	Na5—O37	2.41 (2)
Na3—O26	2.32 (2)	Na5—O19	2.42 (1)
Na3—O27	2.35 (2)	Na5—O25	2.42 (2)
Na3—O29	2.39 (1)	Na5—O22	2.43 (2)
N1···O7	2.85 (2)	N1···O16	3.04 (2)
N1···O18$^{\text{vi}}$	2.98 (2)	N1···O13	3.16 (2)
N1···O27$^{\text{viii}}$	2.98 (2)	N1···O26$^{\text{viii}}$	3.26 (2)

Symmetry codes: (i) $2-x, 1-y, -z$; (ii) $2-x, 1-y, 1-z$; (iii) $1+x, y, -1+z$; (iv) $2-x, 2-y, -z$; (v) $-1+x, 1+y, z$; (vi) $1-x, 1-y, 1-z$; (vii) $1-x, 2-y, 1-z$; (viii) $1+x, -1+y, z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1268). Services for accessing these data are described at the back of the journal.

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