INORGANIC COMPOUNDS

$(NH_4)_2Na_3(V_3W_3O_{19}).12H_2O$

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Abstract

$(NH_4)_2Na_3(V_3W_3O_{19}).12H_2O$, diammonium trisodium nonadecaoxo(tritungsto)trivanadate dodecahydrate, is a mixed V/W salt in which each site has an approximately equal population of V and W atoms. The centrosymmetric polyanion consists of six (V/W)O_6 edge-sharing distorted octahedra and has a well established structure. Each of the three Na^+ cations is surrounded by six water molecules in a distorted octahedron. The (V/W)—O distances are between 1.644 (14) and 2.2885 (10) Å.

Comment

Mixed V/W heteropoly and isopoly compounds, for example $(CH_6N_3)_4V_2W_4O_{19}.16H_2O$ (Nishikawa *et al.*, 1975*a*), $K_7[(V)V_4W_8O_{40}].12H_2O$ (Nishikawa *et al.*, 1975*b*), $K_8(H_2W_{11}V^{IV}O_{40}).13H_2O$ and $(NH_4)_{7.5}H_{0.5}$-$(H_2W_{11}V^{IV}O_{40}).15H_2O$ (Flynn & Pope, 1973), have been reported. We report here the single-crystal structure of the mixed V/W compound $(NH_4)_2Na_3(V_3W_3O_{19}).$-$12H_2O$, (I). The six metal (*M*) positions in the structure are occupied by three V and three W atoms, with the V and W atoms randomly disposed in approximately equal proportions on all sites.

$$2NH_4^+.3Na^- \left[O=M \begin{array}{c} O \\ \| \\ O \end{array} \right]^{5-} .12H_2O$$

(I)
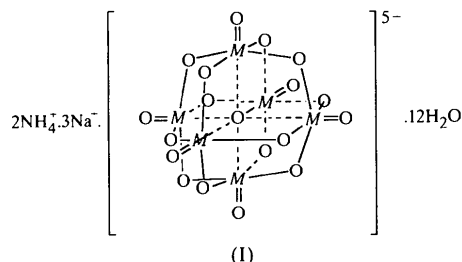
The structure of the $[V_3W_3O_{19}]^{5-}$ polyanion is similar to those of the polyanions $[W_6O_{19}]^{2-}$ (Triki *et al.*, 1991, 1992, 1993) and $[V_2W_4O_{19}]^{4-}$ (Nishikawa

et al., 1975*a*). It consists of a central O atom O_c (O7) surrounded octahedrally by six metal atoms which are bonded to one another through bridging O atoms O_b (O1, O2, O3, O4, O5 and O6, and their symmetry-related atoms). One terminal O atom O_t (O8, O9 and O10, and their symmetry-related atoms) is bonded to each metal atom. The structure of the $[V_3W_3O_{19}]^{5-}$ polyanion can be described as a condensation of six distorted MO_6 octahedra sharing common vertices at the central O atom (O7), which is located on a crystallographic centre of symmetry. Each MO_6 octahedron has common edges with four neighbours. The M—O distances are: $M—O_t$ 1.644 (14)–1.653 (12), $M—O_b$ 1.855 (11)–1.936 (11) and $M—O_c$ 2.267–2.2885 (10) Å. The $M\cdots M$ distances are in the range 3.200 (2)–3.228 (2) Å. The M—O and $M\cdots M$ distances are comparable with the corresponding distances found in the polyanions $[W_6O_{19}]^{2-}$ (Triki *et al.*, 1991, 1992, 1993) and $[V_2W_4O_{19}]^{4-}$ (Nishikawa *et al.*, 1975*a*).

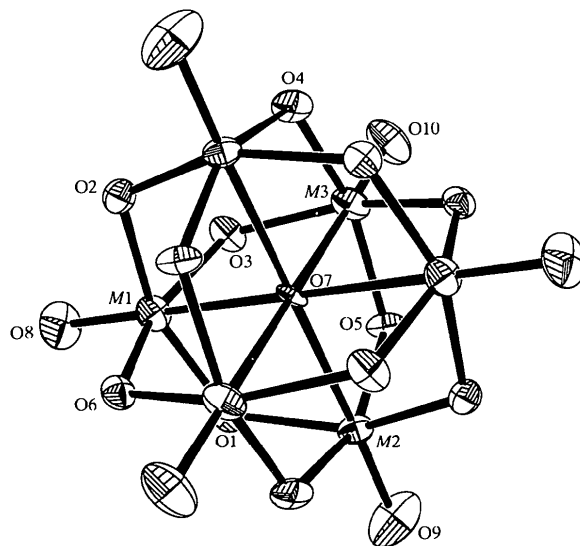Each Na^+ cation is coordinated by six water molecules, with Na—O distances between 2.29 (2) and 2.53 (2) Å.

Fig. 1. The structure of the $[V_3W_3O_{19}]^{5-}$ anion drawn with 50% probability displacement ellipsoids. The six metal (*M*) positions are randomly occupied by three V and three W atoms.

Experimental

The title compound was synthesized by a hydrothermal method. A mixture of NH_4VO_3, Na_2WO_4, NaOH and H_2O (pH 7.5) was sealed in a 15 ml Teflon-lined reactor and kept at 433 K for 7 d. On cooling to room temperature, a brown solution resulted. After standing for 2 d, orange single crystals suitable for X-ray diffraction studies were obtained.

Crystal data

$(NH_4)_2Na_3(V_3W_3O_{19})$.-
12H$_2$O
$M_r = 1329.62$
Triclinic
$P\bar{1}$
$a = 9.190\,(5)$ Å
$b = 9.232\,(2)$ Å
$c = 9.660\,(2)$ Å
$\alpha = 79.150\,(10)°$
$\beta = 85.82\,(3)°$
$\gamma = 65.39\,(4)°$
$V = 731.8\,(5)$ Å^3
$Z = 1$
$D_x = 3.017$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 30
  reflections
$\theta = 5.42–12.52°$
$\mu = 12.820$ mm^{-1}
$T = 293\,(2)$ K
Prism
$0.22 \times 0.18 \times 0.16$ mm
Orange

Data collection

Siemens $P4$ diffractometer
$\omega–2\theta$ scans
Absorption correction:
  empirical via ψ scans
  (North et al., 1968)
  $T_{min} = 0.064$, $T_{max} = 0.129$
3193 measured reflections
2566 independent reflections
2419 reflections with
  $I > 2\sigma(I)$

$R_{int} = 0.030$
$\theta_{max} = 25°$
$h = -1 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$
3 standard reflections
  every 97 reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.179$
$S = 1.203$
2530 reflections
193 parameters
H atoms not located
$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2$
$+ 44.0663P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.94$ e Å^{-3}
$\Delta\rho_{min} = -3.87$ e Å^{-3}
Extinction correction: none
Scattering factors from
  International Tables for
  Crystallography (Vol. C)

	x	y	z	Ueq
OW2	-0.0640 (17)	0.582 (2)	-0.2943 (17)	0.052 (4)
OW3	-0.076 (2)	0.795 (2)	0.1156 (16)	0.054 (4)
OW4	0.265 (2)	0.840 (2)	0.0501 (16)	0.073 (6)
OW5	-0.340 (2)	0.886 (2)	-0.140 (2)	0.068 (5)
OW6	0.1901 (16)	0.5058 (18)	-0.0147 (15)	0.040 (3)
N	-0.2598 (18)	0.9228 (17)	0.5408 (18)	0.034 (4)

† Site occupancy = 0.48 (1).   ‡ Site occupancy = 0.52 (1).   § Site occupancy = 0.54 (2).   ¶ Site occupancy = 0.46 (2).

Table 2. Selected bond lengths (Å)

M1—O8	1.652 (12)	M2—O4^i	1.920 (11)
M1—O1	1.885 (11)	M2—O1	1.930 (11)
M1—O3	1.889 (11)	M2—O7	2.2885 (10)
M1—O6	1.929 (11)	M3—O10	1.653 (12)
M1—O2	1.936 (11)	M3—O5	1.886 (10)
M1—O7	2.267 (2)	M3—O6^i	1.894 (11)
M2—O9	1.644 (14)	M3—O4	1.921 (12)
M2—O2^i	1.896 (11)	M3—O3	1.921 (11)
M2—O5	1.899 (10)	M3—O7	2.2775 (12)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

The occupancy factors of the V and W atoms on each of the $M1$, $M2$ and $M3$ sites were refined as least-squares parameters, with the sum constrained to be 1.0. The highest peak in the difference map is 2.098 Å from $M1$, 1.256 Å from $M2$, 1.435 Å from O1 and 1.418 Å from O7. The largest hole is 0.872 Å from $M3$, 1.662 Å from O3, 1.345 Å from O5 and 1.771 Å from O10.

Data collection: P4 (Siemens, 1994a). Cell refinement: P4 and XSCANS (Siemens, 1994b). Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1985). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL-Plus (Sheldrick, 1990). Software used to prepare material for publication: SHELXL93.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)

$U_{eq} = (1/3)\sum_i\sum_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	Ueq
W1†	0.24152 (12)	0.66812 (12)	0.44445 (11)	0.0218 (3)
V1‡	0.24152 (12)	0.66812 (12)	0.44445 (11)	0.0218 (3)
W2§	0.48388 (12)	0.61730 (12)	0.69251 (10)	0.0222 (3)
V2¶	0.48388 (12)	0.61730 (12)	0.69251 (10)	0.0222 (3)
W3†	0.41629 (13)	0.31876 (12)	0.63449 (11)	0.0219 (3)
V3‡	0.41629 (13)	0.31876 (12)	0.63449 (11)	0.0219 (3)
Na1	0	1	0	0.046 (3)
Na2	-0.0806 (9)	0.6931 (9)	-0.0919 (8)	0.036 (2)
O1	0.2734 (12)	0.7343 (13)	0.6085 (11)	0.020 (2)
O2	0.3016 (13)	0.5400 (13)	0.2958 (12)	0.021 (2)
O3	0.2183 (13)	0.4895 (13)	0.5596 (12)	0.023 (2)
O4	0.4507 (13)	0.2509 (14)	0.4542 (13)	0.024 (2)
O5	0.4156 (13)	0.4496 (13)	0.7630 (11)	0.019 (2)
O6	0.3585 (13)	0.7853 (13)	0.3416 (11)	0.021 (2)
O7	1/2	1/2	1/2	0.011 (3)
O8	0.0539 (14)	0.7921 (16)	0.4025 (14)	0.036 (3)
O9	0.4680 (17)	0.708 (2)	0.8274 (15)	0.048 (4)
O10	0.3577 (16)	0.1835 (16)	0.7282 (15)	0.038 (3)
OW1	0.0117 (17)	0.8942 (17)	-0.2261 (15)	0.040 (3)

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Diaquacobalt Tetracyanonickelate Tetrahydrate

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Abstract

The synthesis and crystal structure of diaquacobalt tetracyanonickelate tetrahydrate are reported. The structure of $Co(H_2O)_2Ni(CN)_4.4H_2O$ is composed of alternating metal cyanide sheets and layers of hydrogen-bonded water molecules. The title compound is isostructural with $Cd(H_2O)_2Ni(CN)_4.4H_2O$.

Comment

Many examples of two-dimensional structures composed of square-planar $M(CN)_4$ (M = Ni, Pd, Pt) units linked to octahedral metal centers by coordination through the cyanide N atom have been reported (Iwamoto *et al.*, 1968) since the discovery of Hofmann's clathrate, $Ni(NH_3)_2Ni(CN)_4.C_6H_6$ (Hofmann & Kuspert, 1897). Most of these compounds contain ammonia or amines coordinated to the octahedral metal center to complete its coordination. A few examples are known which contain coordinated water molecules, *e.g.* $Ni(CN)_2.3H_2O$ (Mathey & Mazieres, 1974), $Cd(H_2O)_2Ni(CN)_4.4H_2O$ (Ham *et al.*, 1993) and $Fe(H_2O)_2Ni(CN)_4.2C_4H_8O_2$ (Kitazawa *et al.*, 1994), or clathrated water molecules, *e.g.* $Cd(NH_3)_2Ni(CN)_4.0.5H_2O$ (Kappenstein & Cernak, 1987) and $Ni(NH_3)_2Ni(CN)_4.0.5H_2O$ (Rayner & Powell, 1958). The new compound $Co(H_2O)_2Ni(CN)_4.4H_2O$ reported here is isostructural with $Cd(H_2O)_2Ni(CN)_4.4H_2O$.

The structure of $Co(H_2O)_2Ni(CN)_4.4H_2O$ is shown in Fig. 1. The structure is composed of alternating metal cyanide sheets and layers of hydrogen-bonded water molecules that alternate along the *a* axis. The metal

cyanide layers are displaced relative to each other so that the axial water molecules bound to the octahedral cobalt ions point towards the center of the square in the square-planar Ni—CN—Co array. Adjacent layers are related by a 2_1 screw axis along **b** as noted by Ham *et al.* (1993). The inter-sheet distance is *a*/2 (6.09 Å). The cyanide layers are not planar but undulate because the $Ni(CN)_4^{2-}$ units alternate along **b** above and below a plane defined by the cobalt ions. The Ni—C bond lengths of 1.851 (3) and 1.864 (3) Å are nearly identical to the values observed in the Cd compound (1.857, 1.866 Å). The Co—N [2.095 (3), 2.101 (3) Å] and Co—O [2.128 (2) Å] bond lengths are typical of those found in other Co^{2+} coordination compounds (Lu *et al.*, 1997). The shorter Co—*L* distances compared with the corresponding Cd—*L* distances largely account for the smaller unit cell observed for the cobalt phase.
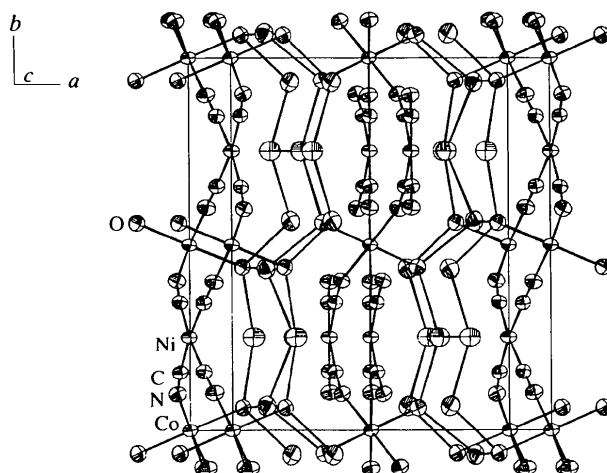

Fig. 1. Perspective view of the arrangement of the $CoNi(CN)_4$ and H_2O sheets. Displacement ellipsoids are drawn at the 50% probability level.
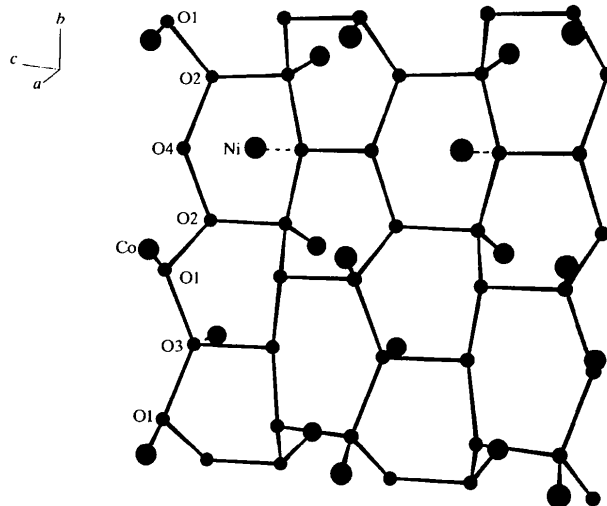

Fig. 2. The arrangement of the network water molecules.