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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{V}-\text{O}) = 0.003\text{ \AA}$
 R factor = 0.036
 wR factor = 0.096
Data-to-parameter ratio = 15.6For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Dipotassium bis[hexaaquacobalt(II)]
decavanadate tetrahydrate

The title compound, $\text{K}_2[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]_2[\text{V}_{10}\text{O}_{28}]\cdot 4\text{H}_2\text{O}$, was obtained by reacting CoCl_2 with KVO_3 and it was found to crystallize in the triclinic system in space group $P\bar{1}$. The $\text{V}\cdots\text{V}$ distances are in the range 3.050 (1)–3.291 (2) Å; the four types of $\text{V}-\text{O}$ bond length are in the ranges 1.604 (3)–1.608 (3) (Ot), 1.902 (3)–2.006 (3) (Oc), 1.678 (3)–2.054 (3) (Ob) and 2.105 (3)–2.342 (3) Å (Oh).

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Comment

The decavanadate anion, $[\text{V}_{10}\text{O}_{28}]^{6-}$, is a very stable and typical isopolyanion species of vanadium. Since its structure was reported by Evans (1966), crystal structures of many salts have been characterized, *e.g.* $\text{K}_2[\text{Zn}(\text{H}_2\text{O})_6]_2[\text{V}_{10}\text{O}_{28}]\cdot 4\text{H}_2\text{O}$ (Evans, 1966), $(\text{NH}_4)_2[\text{Co}_2[\text{V}_{10}\text{O}_{28}]\cdot 16\text{H}_2\text{O}$ (Nowogrocki *et al.*, 1997), $[\text{Na}(\text{H}_2\text{O})_3]_2[\text{Ni}(\text{H}_2\text{O})_2][\text{V}_{10}\text{O}_{28}]\cdot 4\text{H}_2\text{O}$, (Higami *et al.*, 2002), and $\text{Na}_4[\text{Ni}(\text{H}_2\text{O})_6][[\text{V}_{10}\text{O}_{28}]\cdot 17\text{H}_2\text{O}$ (Sun *et al.*, 2002), containing both transition metal complex and alkali metal (or ammonium) cations. The structure of the title compound, $\text{K}_2[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]_2[\text{V}_{10}\text{O}_{28}]\cdot 4\text{H}_2\text{O}$, (I), is isostructural with $\text{K}_2[\text{Zn}(\text{H}_2\text{O})_6]_2[\text{V}_{10}\text{O}_{28}]\cdot 4\text{H}_2\text{O}$ (Evans, 1966).

The configuration of the polyanion is shown in Fig. 1. The centrosymmetric polyanion consists of five independent $[\text{VO}_6]$ octahedra sharing edges and has approximate D_{2h} symmetry. The O atoms in the anion can be divided into four groups by the type of coordination, *viz.* Ot, Ob, Oc, and Oh, where Ot represents a terminal O atom bound to a V atom, Ob

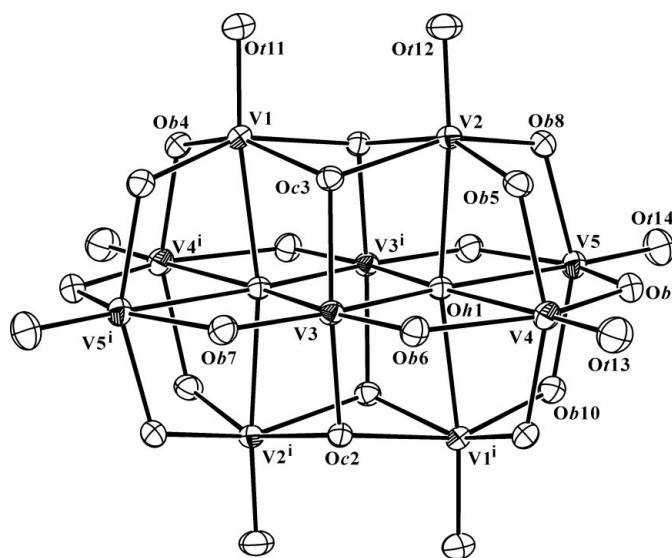


Figure 1

The polyanion structure in $\text{K}_2[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]_2[\text{V}_{10}\text{O}_{28}]\cdot 4\text{H}_2\text{O}$. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (i) $1 - x, 1 - y, 1 - z$.]

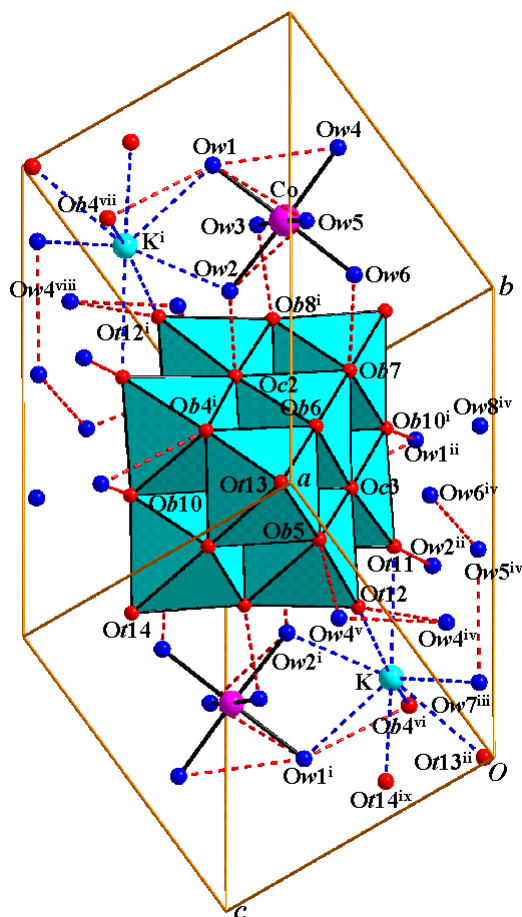


Figure 2
Unit-cell packing of $\text{K}_2[\text{Co}^{\text{II}}(\text{H}_2\text{O})_6]_2[\text{V}_{10}\text{O}_{28}]\cdot 4\text{H}_2\text{O}$. Probable O...O hydrogen bonds are shown in red broken lines. [Symmetry code: (i) $1-x, 1-y, 1-z$; (ii) $-1+x, y, z$; (iii) $x, y, -1+z$; (iv) $1-x, 1-y, -z$; (v) $x, -1+y, z$; (vi) $-x, 1-y, 1-z$; (vii) $1+x, y, z$; (viii) $x, y, 1+z$; (ix) $1-x, -y, 1-z$.]

represents a doubly bridging O atom bound to two V atoms, Oc represents a triply bridging O atom bound to three V atoms, and Oh represents a central O atom coordinated to six V atoms. The V...V distances are in the range 3.050 (1)–3.291 (2) Å; four types of V–O bond length are in the ranges 1.604 (3)–1.608 (3) (Ot), 1.902 (3)–2.006 (3) (Oc), 1.678 (3)–2.054 (3) (Ob) and 2.105 (3)–2.342 (3) Å (Oh). The bond lengths and angles of $[\text{V}_{10}\text{O}_{28}]^{6-}$ show similar trends to those found in the reference literature. The framework of $[\text{V}_{10}\text{O}_{28}]^{6-}$ has been studied in detail previously (Evans, 1966; Nowogrocki *et al.*, 1997).

Fig. 2 shows the crystal packing of (I) with the hydrogen-bonding interactions. All the O atoms of the anion, except Oh1, Oc3, Ob6, Ot13 and Ot14, form hydrogen bonds with water molecules. The $[\text{V}_{10}\text{O}_{28}]^{6-}$ and $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ ions are linked together by strong hydrogen bonds. The Co^{2+} ion is surrounded by six water molecules in the form of a regular octahedron, with distances ranging from 2.072 (3) to 2.111 (3) Å. The K^+ ion is coordinated by eight O atoms, with

distances in the range 2.756 (4)–3.030 (3) Å. A list of hydrogen-bond distances, involving water molecules, less than 3.1 Å is given in Table 2.

Experimental

Compound (I) was obtained by mixing hot aqueous solutions of KVO_3 (0.5 g per 20 ml) and CoCl_2 (0.1 g per 20 ml), and adjusting the pH to about 5.0 with 3M HNO_3 . The solution was concentrated to about 20 ml by heating in a water bath. After a day, crystals of (I) were isolated at room temperature.

Crystal data

$\text{K}_2[\text{Co}(\text{H}_2\text{O})_6]_2[\text{V}_{10}\text{O}_{28}]\cdot 4\text{H}_2\text{O}$
 $M_r = 1441.72$
 Triclinic, $P\bar{1}$
 $a = 10.762$ (2) Å
 $b = 11.122$ (3) Å
 $c = 8.771$ (2) Å
 $\alpha = 105.12$ (2)°
 $\beta = 109.379$ (18)°
 $\gamma = 65.112$ (18)°
 $V = 889.3$ (4) Å³

$Z = 1$
 $D_x = 2.692$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 28 reflections
 $\theta = 9.5$ – 10.4 °
 $\mu = 3.78$ mm⁻¹
 $T = 298$ (2) K
 Plate, pale brown
 $0.13 \times 0.10 \times 0.09$ mm

Data collection

Stoe Stadi-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: numerical (*X-SHAPE*; Stoe & Cie, 1996)
 $T_{\text{min}} = 0.591$, $T_{\text{max}} = 0.704$
 4092 measured reflections
 4092 independent reflections
 3403 reflections with $I > 2\sigma(I)$

$\theta_{\text{max}} = 27.5$ °
 $h = -13 \rightarrow 13$
 $k = -14 \rightarrow 13$
 $l = 0 \rightarrow 11$
 3 standard reflections
 frequency: 60 min
 intensity decay: 3.6%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.096$
 $S = 1.12$
 4092 reflections
 262 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.7547P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.54$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.67$ e Å⁻³

Table 1

Selected geometric parameters (Å).

V1–Oh1 ⁱ	2.241 (2)	V3–Oc3	1.902 (2)
V1–Oc2 ⁱ	2.004 (3)	V3–Ob6	1.678 (3)
V1–Oc3	1.973 (2)	V3–Ob7	1.704 (3)
V1–Ob4	1.826 (3)	V4–Oh1	2.304 (2)
V1–Ob10 ⁱ	1.832 (3)	V4–Ob6	2.054 (3)
V1–Or11	1.608 (3)	V4–Ob4 ⁱ	1.841 (3)
V2–Oh1	2.224 (2)	V4–Ob5	1.908 (3)
V2–Oc2 ⁱ	2.006 (3)	V4–Ob9	1.832 (3)
V2–Oc3	1.992 (3)	V4–Or13	1.604 (3)
V2–Ob5	1.811 (3)	V5–Oh1	2.342 (3)
V2–Ob8	1.836 (3)	V5–Ob7 ⁱ	2.022 (3)
V2–Or12	1.604 (3)	V5–Ob8	1.892 (3)
V3–Oh1	2.105 (2)	V5–Ob9	1.841 (3)
V3–Oh1 ⁱ	2.124 (2)	V5–Ob10	1.870 (3)
V3–Oc2	1.933 (2)	V5–Or14	1.594 (3)

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

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
Ow1—H1b···Ob9 ⁱ	0.93	1.83	2.728 (4)	163
Ow1—H1a···Ob10 ⁱⁱ	0.93	2.01	2.925 (4)	166
Ow1—H1b···Ow4	0.93	2.79	2.950 (4)	90
Ow1—H1a···Ow5	0.93	2.99	3.063 (4)	86
Ow1—H1a···Ob4 ⁱⁱⁱ	0.93	2.67	3.069 (4)	107
Ow2—H2a···Oc2	0.85	1.85	2.685 (3)	166
Ow2—H2b···Ow5	1.01	2.63	2.923 (4)	97
Ow2—H2b···Ow7 ⁱⁱⁱ	1.01	2.41	3.063 (4)	122
Ow2—H2b···Or11 ⁱⁱⁱ	1.01	2.04	2.937 (4)	147
Ow3—H3b···Ob8 ⁱ	0.99	1.73	2.702 (4)	167
Ow3—H3a···Ob8 ^{iv}	0.93	1.84	2.763 (4)	167
Ow4—H4b···Ob5 ⁱ	0.86	1.99	2.749 (4)	147
Ow4—H4b···Ow4 ^v	0.86	2.59	3.041 (6)	114
Ow4—H4a···Ow8 ^{vi}	0.93	2.08	2.949 (5)	154
Ow4—H4a···Or12 ^{vi}	0.93	2.76	3.060 (4)	100
Ow5—H5b···Ow7 ⁱⁱⁱ	0.88	2.08	2.889 (5)	152
Ow6—H6b···Ob7	0.91	1.91	2.804 (4)	170
Ow7—H7b···Ob10 ^{vii}	0.96	2.04	2.958 (4)	160

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

All H atoms were located in a difference Fourier map and refined as riding on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. The highest

peak in the difference map is 1.26 Å from H5b and the largest hole is 0.80 Å from V3.

Data collection: *Stadi4* (Stoe & Cie, 1996); cell refinement: *Stadi4*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1998); software used to prepare material for publication: *SHELXL97*.

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