Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A hydrated ethylenediammonium salt of a new polymeric polyoxoanion: $(H_2en)_4[Co(H_2O)_2(OH)_2(VO)_6(HPO_4)_4(PO_4)_4]\cdot 3H_2O$

Guo-You Luan *et al.*

Electronic paper
This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A hydrated ethylenediammonium salt of a new polymeric polyoxoanion: $(H_2en)_4[Co(H_2O)_2(OH)_2(VO)_6(HPO_4)_4(PO_4)_4]\cdot 3H_2O$

Guo-You Luan, En-Bo Wang,* Wan-Sheng You, Lin Xu and Qin-Lin He

Department of Chemistry, Northeast Normal University, Changchun, Jilin 130024, People's Republic of China
Correspondence e-mail: huchw@nenu.edu.cn

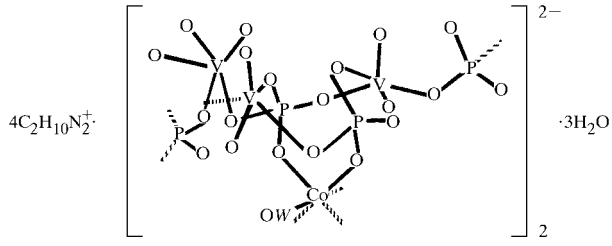
Received 10 May 2000
Accepted 26 May 2000

Data validation number: IUC0000151

The title compound, tetrakis(ethylenediammonium) tetra-μ-hydrogenphosphato-di-μ-hydroxo- tetra-μ-phosphato-bis(-aquacobalt)hexakis(oxovanadium) trihydrate, was synthesized hydrothermally at moderate temperature. The structure consists of diprotonated ethylenediammonium cations and layers of the polyanions. The polyanion contains four PO_4 tetrahedra and three VO_5 square pyramids that are linked through corner-sharing by alternating P—O—V, which gives rise to a chain. The chains, connected by $CoO_4(H_2O)_2$ octahedra, form layers, resulting in a two-dimensional layered structure. The Co—O distances are in the range 1.984 (3)–2.038 (4) Å, the P—O distances 1.508 (3)–1.575 (3) Å and the V—O distances 1.585 (3)–2.010 (3) Å.

Comment

Structures similar to the title compound that have been reported are as follows: $[(VO)_3(H_2O)_2(PO_4)_2(HPO_4)]^{2-}$ (Lu *et al.*, 1998), $[(VO)_2(PO_4)_2]^{2-}$, $[VO]_3(HPO_4)_2(PO_4)_2]^{4-}$ (Soghomonian *et al.*, 1994), $[V(OH)(PO_4)_2(H_2)]^-$ (Soghomonian *et al.*, 1998), $[VO_4(OH)_4(PO_4)_2]^{2-}$, $[(VO)_5(OH)_2(PO_4)_4]^{2-}$, $[(VO)_8(HPO_4)_3(PO_4)_4(OH)_2]^{4-}$,$[(VO)_3(OH)_2(PO_4)_2]^{2-}$ (Soghomonian *et al.*, 1995), $[(VO)V(HPO_4)_3(H_2O)_2]^-$ (Haushalter *et al.*, 1993), $[V(H_2O)_2(VO)_8(OH)_4(HPO_4)_4(PO_4)_4(H_2O)_2]^{5-}$ (Soghomonian *et al.*, 1993) and $[(VO)_3(PO_4)(HPO_4)]^{2-}$ (Bircsak *et al.*, 1998). The polyanion structure of the title compound, (I), consists of $\{V_3P_4\}$ basic units, which are built up from PO_4 tetrahedra and VO_5 square pyramids in a corner-sharing linkage mode, leading to a one-dimensional chain. The connection of P2—O8—V3—O20—P4—O9—V2—O1—P2 gives rise to an eight-membered ring in which P2 links P2—O2—V1—O4—P1 and V3 links V3—O3—P3; thus, an infinite one-dimensional chain is formed. The chains are connected by $CoO_4(H_2O)_2$ octahedra resulting in the formation of layers of the polyanions. Connecting Co with P—V—O also produces two eight-membered rings, namely Co—O13—P4—O20—V3—O8—P2—O14—Co and Co—O13—P4—O9—V2—P2—O14—Co. The PO_4 tetrahedra are slightly distorted, with P—O distances ranging from 1.057 to 1.575 Å and angles from 105.7 (2) to 113.3 (2)°. The VO_5 square pyramids are also distorted, with V—O distances in the ring of 1.585 (3)–2.010 (3) Å and angles of 104.3 (2)–108.0 (2)°, in addition, the geometry within the $CoO_4(H_2O)_2$ octahedra are as follows: Co—O13 2.038 (4) Å, Co—O14 1.984 (3) Å and Co—O*W*3 2.056 (5) Å; O14*A*—Co—O14, O*W*3*A*—Co—O*W*3 and O13—Co—O13*A* are all 180°, while the remaining angles are in the range 85.1 (2)–94.9 (2)°; therefore, the title compound



(I)

exhibits a two-dimensional layered structure constructed from diprotonated ethylenediammonium cations, $(H_2en)^{2+}$, and the polyanion $[Co(H_2O)_2(OH)_2(VO)_6(HPO_4)_4(PO_4)_4]^{8-}$, with the organic ammonium cations and water molecules intercalated between the layers.

Experimental

The synthesis of the title compound was carried out by hydrothermal reaction of ethylenediamine, V_2O_5, H_3PO_4, $CoCl_2.6H_2O$ and H_2O (molar ratio 5:8:5:1:1000) in a 25 ml acid-digestion bomb at 413 K for 5 d. Blue crystals were isolated from solution after cooling to room temperature.

Crystal data

$(C_2H_{10}N_2)_4[Co(H_2O)_2(OH)_2(VO)_6(HPO_4)_4(PO_4)_4]\cdot 3H_2O$
M_r = 1596.94
Monoclinic, $C2/c$
a = 20.709 (4) Å
b = 9.968 (2) Å
c = 23.660 (5) Å
β = 101.04 (3)°
V = 4793.7 (17) Å^3
Z = 4
D_x = 2.213 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 5.02–10.92°
μ = 1.855 mm^{-1}
T = 293 (2) K
Block, blue
0.50 × 0.40 × 0.38 mm

Data collection

Siemens *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical (North *et al.*, 1968)
T_{min} = 0.359, T_{max} = 0.494
5341 measured reflections
4207 independent reflections
3501 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 25°
$h = -1 \rightarrow 24$
$k = -1 \rightarrow 11$
$l = -28 \rightarrow 27$
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.137
S = 1.123
4207 reflections
336 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0913P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 1.80 e Å^{-3}
$\Delta\rho_{min}$ = −1.69 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co—O14	1.984 (3)	V3—O8	2.002 (3)
Co—O13	2.038 (4)	V3—O3	2.010 (3)
Co—O*W*3	2.056 (5)	P1—O6	1.529 (3)
V1—O11	1.586 (3)	P1—O4	1.541 (3)
V1—O12	1.966 (3)	P2—O8	1.528 (3)
V1—O7	1.971 (3)	P2—O14	1.532 (3)
V1—O4	1.979 (3)	P2—O1	1.542 (3)
V1—O2	1.985 (3)	P2—O2	1.544 (3)
V2—O16	1.586 (3)	P3—O10	1.513 (3)
V2—O5	1.966 (3)	P3—O3	1.531 (3)
V2—O9	1.999 (3)	P3—O18	1.575 (3)
V2—O1	2.009 (3)	P4—O20	1.508 (3)
V3—O19	1.585 (3)	P4—O9	1.522 (3)
V3—O20	1.940 (3)	P4—O13	1.536 (4)
V3—O15	1.987 (3)	P4—O17	1.551 (3)
O14—Co—O13	92.27 (14)	O15—V3—O3	84.72 (13)
O14—Co—O*W*3	85.14 (15)	O8—V3—O3	150.00 (13)
O13—Co—O*W*3	90.5 (2)	O6—P1—O4	109.7 (2)
O11—V1—O12	107.7 (2)	O8—P2—O14	113.3 (2)
O11—V1—O7	104.7 (2)	O8—P2—O1	110.6 (2)
O12—V1—O7	85.49 (13)	O14—P2—O1	107.9 (2)
O11—V1—O4	108.0 (2)	O8—P2—O2	107.7 (2)
O12—V1—O4	144.23 (14)	O14—P2—O2	106.0 (2)
O7—V1—O4	88.07 (13)	O1—P2—O2	111.3 (2)
O11—V1—O2	104.3 (2)	O10—P3—O3	111.9 (2)
O12—V1—O2	86.42 (12)	O10—P3—O18	106.4 (2)
O7—V1—O2	150.92 (14)	O3—P3—O18	110.2 (2)
O4—V1—O2	82.37 (12)	O20—P4—O9	111.4 (2)
O16—V2—O5	107.3 (2)	O20—P4—O13	109.9 (2)
O16—V2—O9	102.9 (2)	O9—P4—O13	112.0 (2)
O5—V2—O9	81.41 (13)	O20—P4—O17	107.8 (2)
O16—V2—O1	104.2 (2)	O9—P4—O17	109.7 (2)
O5—V2—O1	148.31 (14)	O13—P4—O17	105.7 (2)
O9—V2—O1	94.64 (12)	P2—O1—V2	120.5 (2)
O19—V3—O20	106.3 (2)	P2—O2—V1	136.1 (2)
O19—V3—O15	107.1 (2)	P3—O3—V3	131.5 (2)
O20—V3—O15	146.51 (13)	P1—O4—V1	134.3 (2)
O19—V3—O8	104.8 (2)	P2—O8—V3	136.6 (2)
O20—V3—O8	88.57 (13)	P4—O9—V2	134.1 (2)
O15—V3—O8	84.47 (13)	P4—O13—Co	132.8 (2)
O19—V3—O3	105.1 (2)	P2—O14—Co	134.0 (2)
O20—V3—O3	85.20 (13)	P4—O20—V3	125.5 (2)

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1995); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); software used to prepare material for publication: *SHELXTL*.

This work was funded by the National Natural Science Foundation of China.

References

Bircsak, Z. & Harrison, W. T. A. (1998). *Inorg. Chem.* **37**, 3204–3208.

Haushalter, R. C., Wang, Z., Thompson, M. E. & Zubieta, J. (1993). *Inorg. Chem.* **32**, 3700–3704.

Lu, Y., Haushaulter, R. C. & Zubieta, J. (1998). *Inorg. Chim. Acta*, **268**, 257–261.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL*93. University of Göttingen, Germany.

Siemens (1994). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Siemens (1995). *SHELXTL Reference Manual.* Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Soghomonian, V., Haushaulter, R. C., Chen, Q. & Zubieta, J. (1994). *Inorg. Chem.* **33**, 1700–1704.

Soghomonian, V., Meyer, L. A., Haushaulter, R. C.& Zubieta, J. (1998). *Inorg. Chim. Acta*, 275–276, 122–129.

Soghomonian, V., Chen, Q., Haushaulter, R. C. & Zubieta, J. (1993). *Angew. Chem. Int. Ed. Engl.* **32**, 610–612.

Soghomonian, V., Chen, Q., Zhang, Y., Haushaulter, R. C., O'Connor, C. J. & Zubieta, J. (1995). *Inorg. Chem.* **34**, 3509–3519.