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catena-Poly[[bis[triaqua[2,5-bis(4-pyridyl)-1,3,4-thiadiazole]cobalt(**II**)]]-μ_4-tetravanadato]

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Key indicators

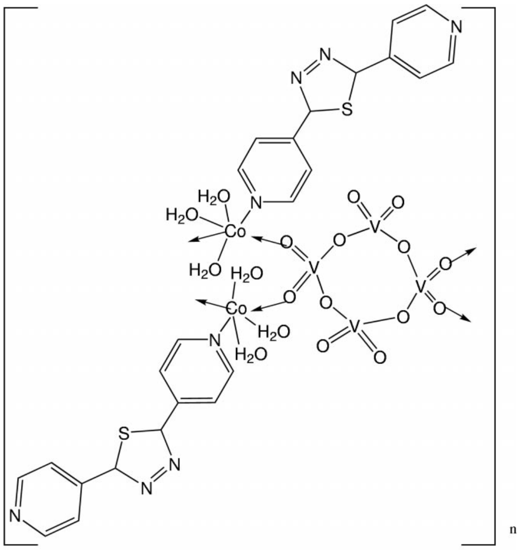
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.039
wR factor = 0.094
Data-to-parameter ratio = 13.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The hydrothermal reaction of cobalt acetate, vanadium pentoxide and 2,5-bis(4-pyridyl)-1,3,4-thiadiazole resulted in the title complex, [Co(V_2O_6)($C_{12}H_8N_4S$)(H_2O)$_3$], in which the cobalt(II) cation shows distorted octahedral geometry, coordinated by one pyridine N atom, two O atoms from tetravanadate and three water molecules.

Comment

There has been considerable interest in the coordination chemistry of oxovanadium polyanions because of their structural diversity and varied physical properties. The equilibria in solution between polyoxovanadium(V) species are complex. The cyclic tetravanadate anion, $(V_4O_{12})^{4-}$, which consists of corner-shared VO_4 tetrahedra, is one of the main oxovanadium species in the pH range 6.5–8 (Zheng *et al.*, 2001; Law *et al.*, 2000). Our studies have shown that the cyclic tetravanadate and linear divanadate can link *via* oxygen sharing to form more complicated V/O polyanions (Zhang *et al.* 2000). Besides the synthetic conditions, the structures of coordination complexes of oxovanadium polyanions are generally influenced by the presence of organic N-containing ligands, for example, 4,4′-bipyridine, 2,2′-bipyridine, 1,10-phenanthroline and 1,2,4-triazole (LaDuca *et al.*, 2000).



(I)

We report here a new coordination complex of the cyclic tetravanadate anion containing the uncommon ligand 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (bpydtz), *viz. catena*-poly[bis[triaquacobalt(II)-di-2,5-bis(4-pyridyl)-1,3,4-thiadiazole]-(tetravanadate)], (I). The asymmetric unit consists of one cobalt(II) ion, one bpydtz molecule, half a tetravanadate

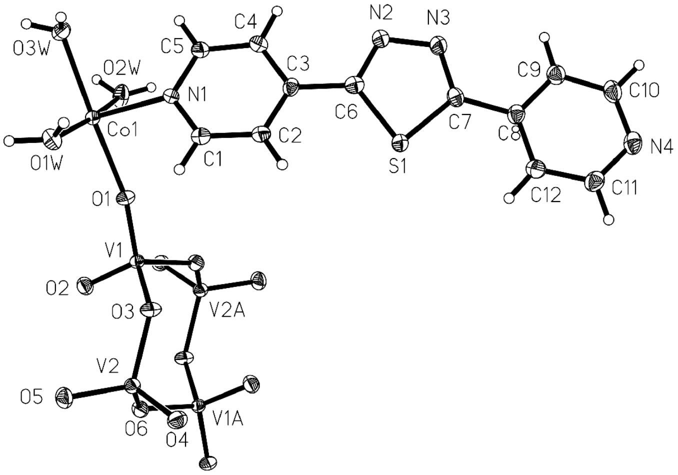


Figure 1
View of a fragment of (I), showing 50% displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii. Atoms with suffix A are generated by the symmetry operation $-x, -1-y, 1-z$.

anion and three water molecules. The Co^{II} species shows distorted octahedral geometry, coordinated by one pyridine N atom, two tetravanadate O atoms and three water molecules (Fig. 1). Although bpydtz has four potential N-donors, only one pyridine N atom is coordinated to cobalt in (I). The tetravanadate anion has a chair-like conformation and is coordinated to four Co^{II} cations, giving to rise to a chain structure, as shown in Fig. 2. The coordinated water molecules and O atoms from tetravanadate participate in hydrogen bonds (Table 2).

Experimental

A mixture of cobalt acetate tetrahydrate (0.100 g, 0.4 mmol), vanadium pentoxide (0.091 g, 0.5 mmol), 2,5-bis(4-pyridyl)-1,3,4-thiadiazole (0.096 g, 0.4 mmol) and water (7 ml) in a molar ratio of 1:1.25:1:970 was sealed in a 15-ml Teflon-lined stainless-steel container, heated to 433 K and held at that temperature for 72 h. After cooling to room temperature, red block-shaped crystals were recovered in 60% yield, based on vanadium. Analysis. Calc. for $C_{12}H_{14}CoN_4O_9SV_2$: C, 26.15; H, 2.56; N, 10.17; S, 5.82. Found: C, 26.11; H, 2.59; N, 10.13; S, 5.77.

Crystal data

$[Co(V_2O_6)(C_{12}H_8N_4S)(H_2O)_3]$
$M_r = 551.14$
Triclinic, $P\overline{1}$
$a = 8.0562\ (18)$ Å
$b = 8.2506\ (18)$ Å
$c = 14.253\ (3)$ Å
$\alpha = 96.313\ (3)°$
$\beta = 91.631\ (3)°$
$\gamma = 103.402\ (3)°$
$V = 914.6\ (3)$ Å^3
$Z = 2$
$D_x = 2.001$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 86 reflections
$\theta = 2.5–25.2°$
$\mu = 2.07$ mm^{-1}
$T = 293\ (2)$ K
Block, red
0.28 × 0.21 × 0.12 mm

Data collection

Bruker SMART APEX CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.595$, $T_{max} = 0.789$
4126 measured reflections
3483 independent reflections
3035 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 26.0°$
$h = -8 \rightarrow 9$
$k = -10 \rightarrow 7$
$l = -14 \rightarrow 17$

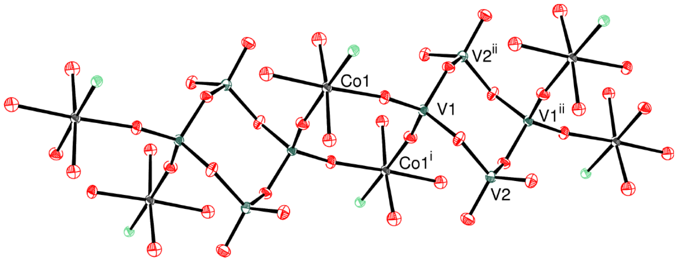


Figure 2
Part of the chain structure of (I). Symmetry codes are as in Table 1. All ligand atoms except N1 and all H atoms are omitted for clarity.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.094$
$S = 1.03$
3483 reflections
262 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.55$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Co1—O2^{i}	2.019 (2)	Co1—O1*W*	2.096 (2)
Co1—O1	2.063 (2)	Co1—N1	2.102 (3)
Co1—O2*W*	2.092 (2)	Co1—O3*W*	2.127 (2)
V1—O1—Co1	165.77 (15)	V1—O3—V2	123.74 (13)
V1—O2—Co1^{i}	168.36 (15)	V1^{ii}—O6—V2	128.55 (13)

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $-x, -1-y, 1-z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*W*—H3*WA*···O4^{iii}	0.92	1.90	2.813 (3)	171
O1*W*—H1*WA*···O3^{iii}	0.90	1.82	2.716 (3)	172
O3*W*—H3*WB*···O6^{i}	0.86	2.23	3.014 (3)	152
O2*W*—H2*WA*···N4^{iv}	0.81	2.03	2.804 (4)	160
O2*W*—H2*WB*···O5^{i}	0.91	2.01	2.916 (3)	176
O1*W*—H1*WB*···O4^{v}	0.94	1.93	2.867 (3)	173

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

The water H-atoms were located in Fourier difference maps. The aromatic H-atoms were placed at calculated positions (C—H = 0.96 Å) and refined in the riding-model approximation. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier atom) was applied in all cases.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*–II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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