

A novel two-dimensional structure containing the first antimony-substituted polyoxovanadium clusters: $[\{\text{Co}(\text{en})_2\}_2\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})] \cdot 6\text{H}_2\text{O}$

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Received 28th June 2002, Accepted 22nd July 2002

First published as an Advance Article on the web 29th July 2002

The novel framework $[\{\text{Co}(\text{en})_2\}_2\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})] \cdot 6\text{H}_2\text{O}$ is composed of two-dimensional arrays of $\{\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})\}$ clusters interlinked via $\{\text{Co}(\text{en})_2\}$ bridging groups; such antimony–vanadium clusters with antimony and vanadium in low oxidation states were previously unknown.

Keggin-type heteropolycompounds find application as heterogeneous catalysts in a variety of oxidation reactions.¹ However, the biggest drawback of heteropolycompounds, which limits their application as heterogeneous catalysts, is the structural decomposition, which occurs in air at temperatures close to 300 °C.² It is interesting that heteropolycompounds containing antimony oxide often play an important role in heterogeneous oxidation catalysis and antimony cations have a stabilizing effect on polyoxometalates at high (>450 °C) temperatures.³ The reports of antimony-containing polyoxometalates are rather scarce. However, some polyoxometalates of antimony-containing polyoxotungstates^{4–9} and antimony-containing polyoxomolybdates¹⁰ have been reported. Here we report the synthesis and X-ray crystal structure analysis of the first antimony-containing polyoxovanadium compound $[\{\text{Co}(\text{en})_2\}_2\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})] \cdot 6\text{H}_2\text{O}$ (**1**).

Compound **1** was synthesized hydrothermally as black rhombus crystals in 46% yield (based on Sb). A mixture of Sb_2O_3 (0.25 g), V_2O_5 (0.30 g), $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.21 g), $\text{CoC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (0.31 g) and H_2O (20 mL) in a molar ratio of 1 : 2 : 2 : 2 : 2 : 1292 was stirred for 120 min and then adjusted to pH = 9.0 using en. It was sealed in a 30 mL Teflon-lined reactor and kept at 160 °C for nine days. $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was used as a reducing agent and it was necessary to maintain the pH of the reaction. After being cooled to room temperature, black rhombus crystals were isolated. The elemental analysis, ICP and IR spectra † in combination with the X-ray single-crystal analysis ‡ confirmed the formula of **1**, $[\{\text{Co}(\text{en})_2\}_2\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})] \cdot 6\text{H}_2\text{O}$.

The 2D extended structure (Fig. 1) of **1** consists of $[\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})]^{4-}$ sphere-like clusters, each one of which is linked to four other neighbouring $[\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})]^{4-}$ units by four $[\text{Co}(\text{en})_2]^{2+}$ bridges, generating a two-dimensional network of $[-\{\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})\}-\mu-\{\text{Co}(\text{en})_2\}-\{\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})\}]_n$ arrays. The octahedral geometry around each cobalt is completed by four nitrogen donors from two en molecules $[\text{Co}-\text{N} = 2.125(7)-2.147(7) \text{ \AA}]$ and two *trans*- μ -oxo groups (O3, O20) $[\text{Co}-\text{O} = 2.106(5), 2.121(5) \text{ \AA}]$. The H_2O molecules occupy the parallelogrammic cavities.

The spherical structure (Fig. 2) of each $[\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})]^{4-}$ cluster consists of 14 condensed vanadium oxygen square pyramids (VO_5) and 8 trigonal pyramids (SbO_3), and includes at its center a statistically disordered H_2O molecule.

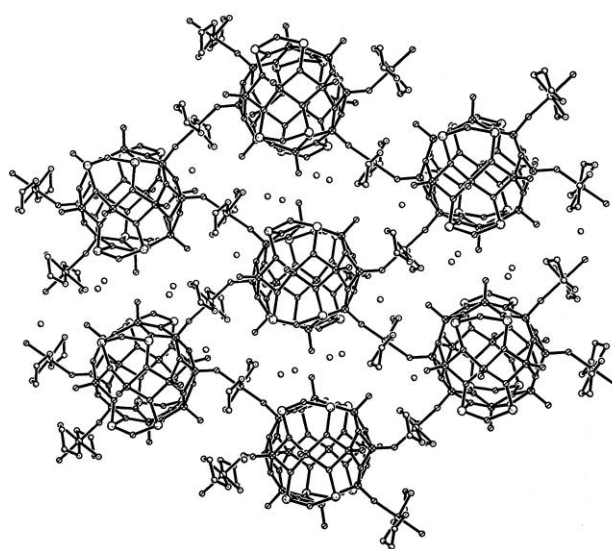


Fig. 1 A view of the extended structure of $[\{\text{Co}(\text{en})_2\}_2\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})] \cdot 6\text{H}_2\text{O}$ showing arrays of $\{\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})\}$ clusters interconnected through $\{\text{Co}(\text{en})_2\}$ bridging groups, with parallelogrammic cavities occupied by the water molecules (open circles). Hydrogen atoms have been omitted.

Two SbO_3 groups are joined together by an oxygen bridge, forming a handle-like Sb_2O_5 moiety. The 14 VO_5 square pyramids are linked with one another through edges, and with SbO_3 groups through vertices. On the one hand, eight vanadium [two V4, two V6, two V1 and two V2] oxygen square pyramids share their opposite edges to form a ring. These vanadium atoms are all co-planar in the plane of the ring within $\pm 0.006 \text{ \AA}$. On the other hand, eight vanadium [two V3, two V4, two V5 and two V7] oxygen square pyramids share their opposite edges to form another ring. These vanadium atoms are all co-planar in the plane of the ring within $\pm 0.009 \text{ \AA}$. Sharing two of the 14 VO_5 square pyramids, the two rings are mutually perpendicular to form a cage. The overall composition of this cage is $[(\text{VO})_{14}\text{O}_{24}]$. The twenty-four oxygen atoms occupy the vertices of a rhombicuboctahedron, which has a total of eighteen square faces. Fourteen of them are formed by the bases of VO_5 square pyramids arranged as described above. The remaining four square faces are formed by the bases of the Sb_2O_5 units to give a total anion composition of $[\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}]^{4-}$. In the Sb_8 compound, the four Sb_2O_5 units occupy four windows of the cage. The shell of $[\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}]^{4-}$ can be considered as a derivative of the spherical cluster shell $[\text{V}_{18}\text{O}_{42}]$.¹¹ Substitution of four VO_5 pyramids of the $[\text{V}_{18}\text{O}_{42}]$

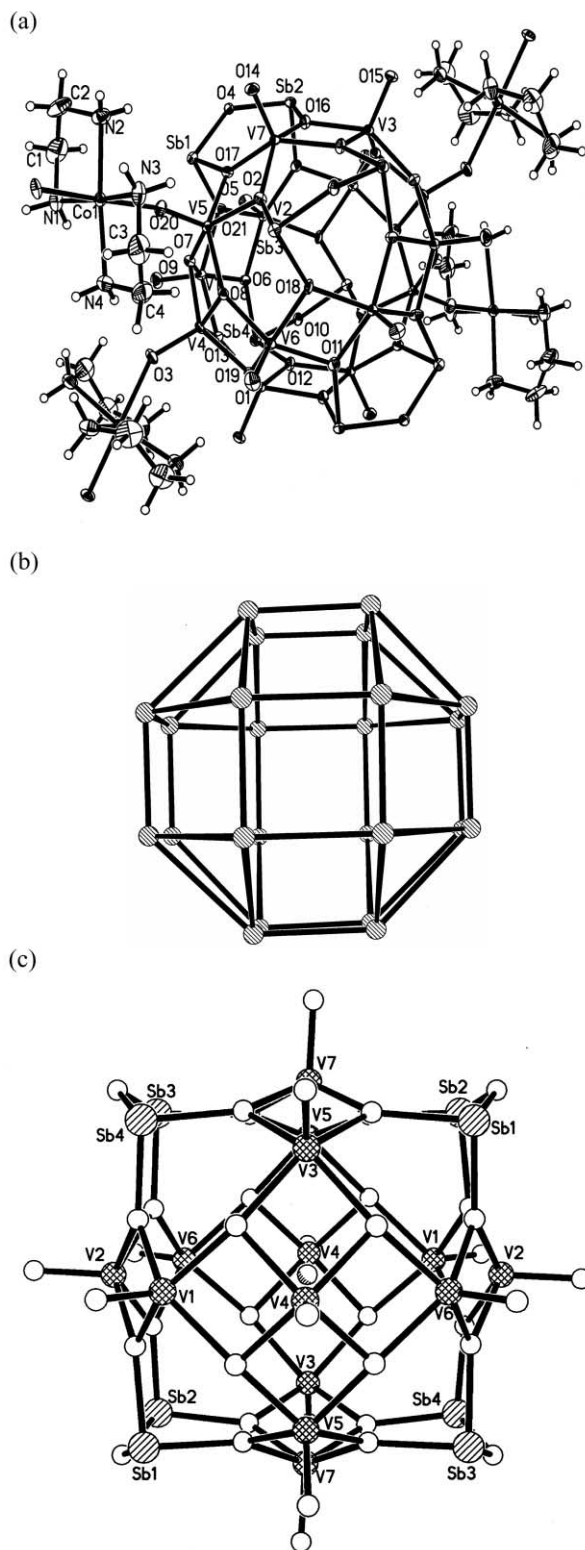


Fig. 2 (a) The building block unit in the crystal structure of $[\{\text{Co}(\text{en})_2\}_2\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})]\cdot 6\text{H}_2\text{O}$ (**1**) showing the atom labelling scheme in the asymmetric unit. Small open circles represent hydrogen atoms. (b) The rhombicuboctahedron spanned by the 24 μ_3 -oxygen atoms of the anion $[\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}]^{4-}$ in **1**. (c) The spherical shell $[\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})]^{4-}$ in **1**. Open circles are oxygen atoms. The four Sb_2O_5 units occupy four windows, which are formed by two eight-membered rings (vertical and horizontal) of square pyramids.

shell by four Sb_2O_5 dimers leads to the $[\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}]^{4-}$ cluster of **1**. The geometry around the square-pyramidal vanadium atoms in $14\{\text{VO}_5\}$ is defined by 24 basal μ_3 -oxygen atoms [$\text{V}-\text{O} = 1.941(5)\text{--}1.990(5)\text{ \AA}$] from the shell, ten terminal oxygen atoms [$\text{V}-\text{O} = 1.601(5)\text{--}1.614(5)\text{ \AA}$], and four apical μ -oxygen atoms ($\text{O}3, \text{O}20$) [$\text{V}-\text{O} = 1.621(5), 1.642(5)\text{ \AA}$]. Each apical μ -oxygen atom is covalently bonded to the cobalt center of the $[\text{Co}(\text{en})_2]^{2+}$ bridge that links two $[\text{Sb}^{\text{III}}_8\text{V}^{\text{IV}}_{14}\text{O}_{42}(\text{H}_2\text{O})]^{4-}$ clusters.

Compound **1** provides an example of connecting antimony–vanadium clusters and transition metal coordination complexes. It suggests that further condensation of clusters into higher dimensional solids through the linkage of $[\text{Co}(\text{en})_2]^{2+}$ groups could be feasible. The bridging Co centers may be substituted by other metal ions (Cu, Cd, Mn, *etc.*) and organometallic groups as evidenced by the ongoing work in our research laboratories.

This work was supported by the National Natural Science Foundation of China and the Research Funds for the Doctoral Program of Higher Education.

Notes and references

† Anal. calc. for $\text{C}_4\text{H}_{23}\text{Co}_1\text{N}_4\text{O}_{24.5}\text{Sb}_4\text{V}_7$: C, 3.38; N, 3.94; H, 1.62; Co, 4.14; V, 25.06; Sb, 34.25%. Found: C, 4.02; N, 3.48; H, 1.28; Co, 3.95; V, 22.98; Sb, 32.87%. IR (KBr/ cm^{-1}): 3469w, 1609s, 978vs, 709s, 598s, 511m, 403s.

‡ Crystal data for **1** $\text{C}_4\text{H}_{23}\text{CoN}_4\text{O}_{24.5}\text{Sb}_4\text{V}_7$: $M = 1421.77$, monoclinic, space group $P2(1)/n$, $a = 14.602(3)$, $b = 12.855(3)$, $c = 17.631(4)\text{ \AA}$, $\beta = 105.80(3)^\circ$, $V = 3184.5(11)\text{ \AA}^3$, $Z = 4$, $D_c = 2.966\text{ g cm}^{-3}$, $\mu = 5.882\text{ mm}^{-1}$. Data collection $1.61 \leq \theta \leq 27.48^\circ$, performed on a Rigaku R-AXIS RAPID IP diffractometer (graphite-monochromated Mo-K α radiation: $\lambda = 0.71073\text{ \AA}$) at 293(2) K. Data processing was by means of the SAINT processing program.¹² The structures were solved by direct methods using the SHELXTL crystallographic software package and refined with full-matrix least-squares.¹³ A total of 13804 reflections were collected of which 7297 were unique ($R_{\text{int}} = 0.0210$). The final R_1 and wR_2 were 0.0371 and 0.0860, respectively, for 404 parameters and 5414 reflections [$I > 2\sigma(I)$]. CCDC reference number 188658. See <http://www.rsc.org/suppdata/dt/b2/b206250j/> for crystallographic data in CIF or other electronic format.

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