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An Organically Templated Cobalt–Vanadium Oxide with β Cage Units: Hydrothermal Synthesis and X-ray Structural Characterization of $(C_2H_{10}N_2)[Co_2(C_2O_4)V_4O_{12}]$

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A novel organically templated cobalt-vanadium oxalate, $(C_2H_{10}N_2)[Co_2(C_2O_4)V_4O_{12}]$, was synthesized under mild hydrothermal conditions and characterized by single-crystal/powder X-ray diffraction, infrared spectroscopy, and thermogravimetric analysis. The compound crystallizes in an orthorhombic system with space group *Cmcm* and cell parameters $a = 11.527(2)$ Å, $b = 9.9476(18)$ Å, $c = 14.780(3)$ Å. The compound possesses 3-dimensional topologies with sodalite analogue structure and is constructed by C_2O_4-incorporated β cage units. On the basis of the results of TG/DTA analyses, the structure is thermally stable up to ~573 K.

Introduction

Inorganic/organic hybrid materials have been extensively studied due to their special properties, especially in living tissues such as hard tissue and dentary.[1,2] Since the inorganic/organic hybrid compounds consist of inorganic and organic compositions, the compounds usually show combined properties of inorganic and organic compositions. In order to obtain new materials with excellent properties in the fields of photochemistry, electromagnetism, catalysis, adsorption, and so on, many attempts have been developed to prepare novel inorganic/organic hybrid compounds. Some materials have been prepared by setting special organic compounds in the inorganic matrix.[3] Recently, a method based on self-organization under hydrothermal conditions has been explored to prepare inorganic/organic hybrid compounds. By this convenient method, many novel inorganic/organic hybrid compounds have been synthesized.[4−7]

It is well-known that by using organic amines as templates many novel microporous materials with new framework topologies have been synthesized.[8−11] These materials include aluminosilicate zeolites, organically templated metal phosphates, aluminophosphate molecular sieves, phosphonates, oxalatophosphates, carboxylates, oxides, and coordination polymers, in which the compositions involve almost all of the elements in the periodic table.[12−14] Most recently, an attempt has been made in our group to prepare novel compounds with inorganic/organic hybrid framework by using organic compounds as templates, and some novel compounds have been prepared.[15−18]

Vanadium systems have been intensively studied due to the variable oxidation states of vanadium (V^{III}, V^{IV}, and V^{V}) and coordination geometries of vanadium oxide polyhedra (tetrahedrons, square pyramids, trigonal bipyramids, and octahedra).[19] This variety leads to an ever-increasing interest

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in the synthesis of new materials with novel structure types. A huge number of vanadylic porous compounds possessing one-, two-, and three-demensional structures are known to date.[16,20,21] The structures of some vanadylic compounds are helical and chiral.[17,22] We try to connect vanadium oxide with organic compounds to prepare some compounds with inorganic/organic hybrid framework structures. By using the complex $[Co(en)_2Cl_2]Cl$ as starting material, a new cobalt−vanadium oxide with an inorganic/organic hybrid framework has been prepared. This compound exhibits three-dimensional sodalite analogue structure, i.e., the structure consists of β cage units, which are the main units in the zeolites A, X, and Y.[23] The similarity between zeolites and inorganic/organic hybrid materials is most interesting in studies for both structures and properties. In this paper, we present the synthesis, single-crystal structure, and physical characterization of this inorganic/organic hybrid cobalt−vanadium oxide, $(C_2H_{10}N_2)[Co_2(C_2O_4)V_4O_{12}]$, which was prepared by using organic amine as structure-directing agent under hydrothermal conditions.

Experimental Section

Synthesis. Black brown crystals of $(C_2H_{10}N_2)[Co_2(C_2O_4)V_4O_{12}]$ were prepared by a two-step reaction. In the first step, $[Co(en)_2Cl_2]Cl$ (0.56 mmol, 0.159 g) was added to a mixture of $H_2C_2O_4{\cdot}2H_2O$ (0.56 mmol, 0.070 g) and distilled water (10.0 mL). The solution was stirred for 1 h and heated in an autoclave at 110 °C for 12 h. A red solution was obtained without crystallization. This solution (solution A) was further used as a reagent for the second step of the synthesis. In the second step, V_2O_5 (0.56 mmol, 0.101 g) and $CH_5N_3{\cdot}HCl$, guanidine hydrochloride (1.11 mmol, 0.106 g) were added to 10.0 mL of solution A. The reaction mixture was stirred for 2 h, sealed in an autoclave, and crystallized at 160 °C for 72 h. The initial pH was ca. 1.8, and the pH of the final liquid phase after hydrothermal reaction was ca. 6.5. The crystalline product was filtered off, washed with distilled water, and dried at ambient temperature.

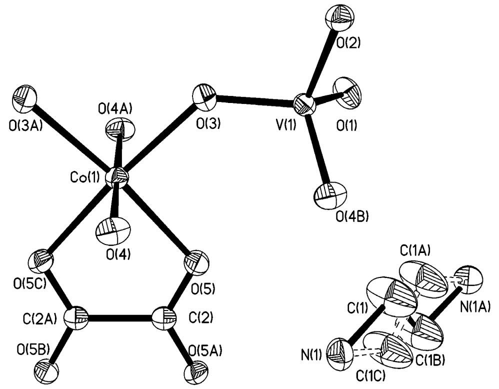

Figure 1. ORTEP drawing of the asymmetric unit of the compound. Thermal ellipsoids are shown at 50% probability.

Table 1. Crystallographic Data for $(C_2H_{10}N_2)[Co_2(C_2O_4)V_4O_{12}]$

emp formula	$C_4H_{10}N_2Co_2V_4O_{16}$	space group	*Cmcm* (No. 63)
a, Å	11.527(2)	T, °C	20(2)
b, Å	9.9476(18)	λ, Å	0.71073
c, Å	14.780(3)	ρ_{calc}, g/cm^3	2.601
V, Å^3	1694.8(6)	μ, mm^{-1}	4.114
Z	4	R1^a $[I > 2\sigma(I)]$	0.0281
fw	663.76	wR2^b $[I > 2\sigma(I)]$	0.0768

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$)^a for $(C_2H_{10}N_2)[Co_2(C_2O_4)V_4O_{12}]$

	x	y	z	U(eq)
V(1)	3578(1)	2375(1)	3639(1)	14(1)
Co(1)	2344(1)	0	5000	16(1)
O(1)	3276(3)	1917(4)	2500	25(1)
O(2)	5000	3085(4)	3689(2)	20(1)
O(3)	3573(2)	992(3)	4264(2)	20(1)
O(4)	2369(2)	1529(3)	5978(2)	23(1)
O(5)	965(2)	976(2)	4368(2)	21(1)
C(1)	478(9)	3530(13)	2811(6)	60(3)
C(2)	0	556(5)	4635(3)	17(1)
N(1)	0	3568(5)	3781(3)	28(1)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Determination of Crystal Structure. A single crystal of the compound with size 0.4 × 0.2 × 0.2 mm was carefully selected under a microscope. A single-crystal structure analysis was performed on a Siemens SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The data were collected at a temperature of 293 ± 2 K. Data processing was accomplished with the SAINT processing program.[24] The structure was solved by direct methods using the SHELXTL crystallographic software package.[25] Charge balancing requirements necessitated the fully protonated ethylenediamine (en). Each C atom of en in the compound occupies two split positions: C_1-C_{1C} and $C_{1A}-C_{1B}$, and each C atom has an occupancy of 0.5. $N_1-C_1-C_{1B}-N_{1A}$ is one split position of the en molecule, and $N_1-C_{1C}-C_{1A}-N_{1A}$ is another split position of the en molecule (Figure 1). Hydrogen positions for the compound were not located for the two C atoms of en in the compound occupy two split positions. All non-hydrogen atoms were refined anisotropically. Details of the final refinements are given in Table 1, and the atomic coordinates and bond distances and bond angles are listed in Tables 2 and 3, respectively.

Characterization. Powder X-ray data were collected on a Siemens D5005 diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). Data were collected in the range $4° \leq 2\theta \leq 120°$. Infrared spectra were collected on a Nicolet Impact 410 instrument using the KBr pellet technique with the range 400−4000 cm^{-1}. TG and DTA data were recorded on Netzsch STA 449C in air and in nitrogen gas with a rate of temperature increase of 10 °C·min^{-1}.

Results and Discussion

Synthesis. In our synthesis of the title compound, the kinds of starting reactants, the synthesis method, and the pH of the initial mixture are main factors influencing the quality and formation of product. We could not obtain the title compound when $[Co(en)_2Cl_2]Cl$ was replaced by $CoCl_2$ or Co_2O_3 in the reaction mixture. This is due to the difference

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for $(C_2H_{10}N_2)[Co_2(C_2O_4)V_4O_{12}]$[a]

V(1)−O(1)	1.7790(14)	O(1)−V(1)#3	1.7790(14)
V(1)−O(2)	1.7859(15)	O(2)−V(1)#4	1.7859(15)
V(1)−O(3)	1.657(3)	O(4)−V(1)#1	1.643(3)
V(1)−O(4)#1	1.643(3)	O(5)−C(2)	1.252(3)
Co(1)−O(3)	2.041(3)	C(1)−C(1)#6	1.434(19)
Co(1)−O(3)#2	2.041(3)	C(1)−N(1)	1.536(10)
Co(1)−O(4)	2.099(3)	C(2)−O(5)#5	1.252(3)
Co(1)−O(4)#2	2.099(3)	C(2)−C(2)#7	1.545(10)
Co(1)−O(5)	2.084(3)	N(1)−C(1)#5	1.536(10)
Co(1)−O(5)#2	2.084(3)		
O(1)−V(1)−O(2)	108.63(17)	O(4)−Co(1)−O(4)#2	178.41(14)
O(3)−V(1)−O(1)	108.31(16)	O(5)−Co(1)−O(4)	88.95(10)
O(3)−V(1)−O(2)	108.00(14)	O(5)−Co(1)−O(4)#2	92.26(10)
O(4)#1−V(1)−O(1)	111.42(17)	O(5)#2−Co(1)−O(4)	92.26(10)
O(4)#1−V(1)−O(2)	109.49(14)	O(5)#2−Co(1)−O(4)#2	88.95(10)
O(4)#1−V(1)−O(3)	110.89(13)	O(5)#2−Co(1)−O(5)	80.58(13)
O(3)−Co(1)−O(4)	90.40(10)	V(1)−O(1)−V(1)#3	142.4(2)
O(3)−Co(1)−O(4)#2	88.49(10)	V(1)−O(2)−V(1)#4	133.2(2)
O(3)−Co(1)−O(5)	93.75(10)	V(1)−O(3)−Co(1)	134.51(14)
O(3)−Co(1)−O(5)#2	173.68(10)	V(1)#1−O(4)−Co(1)	135.11(15)
O(3)#2−Co(1)−O(3)	92.05(14)	C(1)#6 −C(1)−N(1)	108.8(11)
O(3)#2−Co(1)−O(4)	88.49(10)	C(2)−O(5)−Co(1)	112.4(3)
O(3)#2−Co(1)−O(4)#2	90.40(10)	O(5)−C(2)−C(2)#7	117.3(2)
O(3)#2−Co(1)−O(5)	173.68(10)	O(5)#5−C(2)−C(2)#7	117.3(2)
O(3)#2−Co(1)−O(5)#2	93.75(10)	O(5)#5−C(2)−O(5)	125.3(5)

[a] Symmetry transformations used to generate equivalent atoms: #1, $-x + {}^{1}/_{2}, -y + {}^{1}/_{2}, -z + 1$; #2, $x, -y, -z + 1$; #3, $x, y, -z + {}^{1}/_{2}$; #4, $-x + 1, y, z$; #5, $-x, y, z$; #6, $-x, y, -z + {}^{1}/_{2}$; #7, $-x, -y, -z + 1$.

of the structure between $[Co(en)_2Cl_2]Cl$ and $CoCl_2$ and Co_2O_3. The four coordinate sites of the cobalt octahedron are occupied by two en molecules in $[Co(en)_2Cl_2]Cl$, but this structure does not exist in $CoCl_2$ and Co_2O_3. The special structure of $[Co(en)_2Cl_2]Cl$ makes the $C_2O_4^{2-}$ coordinate selectively with the cobalt center. Experimentally, we used a two-step crystallization procedure which favors the formation of final product. However, only a small amount of the title compound can be synthesized when we use a one-step method in the reaction with the same reactants. The action of the starting reactant, $CH_5N_3{\cdot}HCl$, is regulating the pH of the initial mixture. The molar ratio of en and $H_2C_2O_4{\cdot}2H_2O$ in the initial mixture is 2:1, but that in the final crystalline product is 1:1. Some en molecules dissolved in the final liquid phase, so the pH of the reaction system changed from ca. 1.8 to ca. 6.5.

Structure. The structure of the title compound, which shows four-membered- and six-membered-ring channels connected by VO_4 tetrahedrons and CoO_6 octahedra as well as C_2O_4, is a novel three-dimensional inorganic/organic hybrid porous structure derived from a simple building unit. The asymmetric unit in the structure of the title compound is shown in Figure 1. The VO_4 inorganic unit and C_2O_4 organic unit are connected together by using a Co atom as a bridge.

The characteristic basic building unit in the structure of this compound is a distorted sodalite cage, i.e., β cage (Figure 2a), which contains corner-sharing VO_4 tetrahedrons and CoO_6 octahedra as well as the C_2O_4 group. The sodalite cage units are connected with each other via 4-ring windows or 6-ring windows and form 3-dimensional topologies. This β cage unit is made up of six distinct 4-ring windows (two pairs of V_2Co_2 and a pair of V_4) and eight 6-ring windows of four distinct types (three pairs of 6R, V_4Co_2; a pair of $6R_1$, $V_4Co_2C_2O_4$). We can describe the cage as a C_2O_4-incorporated β cage. The protonated ethylenediamine molecules are located in the cages. The maximum cavity diameter measured between the oxygen atoms of the β cage is ∼11.299 Å. The topology of the cages along the (100) plane is shown in Figure 2b. The vanadium atoms of the structure only show a VO_4 tetrahedron coordination state. A VO_4 tetrahedron has four oxygen atoms at distances in the range 1.648(3)−1.7906(16) Å (average $V-O_{av}$ = 1.7220(58) Å). Two *oxo* groups from each VO_4 tetrahedron are used to bridge two VO_4 tetrahedrons from one 4-ring window with O−V−O angles in the range 107.85(15)−111.23(18)° (average $O-V-O_{av}$ = 109.46(00)°), and the other two *oxo* groups are connected with two cobalt atoms coming from two different 6-ring windows, with an average V−O−Co bond angle of 134.71(66)°. Bond length and bond strength were calculated on the basis of the method reported by Brown and Shannon[26] and the data reported by Brown and Altermatt.[27] The bond valence sum calculation assuming $V^{V}-O$ bonds gives BVS values of 5.06 indicating charge ordering. This is confirmed by its coordination state. The cobalt center is coordinated by two oxygen donors from the bidentate oxalate group with the same Co−O bond length of 2.093(3) Å, and four oxygen atoms from four VO_4 tetrahedrons with an average Co−O bond length of 2.074(8) Å. The four VO_4 tetrahedrons come from four different 4-ring windows. The tetradentate oxalate group acts as a chelating unit, connecting exclusively the two cobalt atoms. Extensive bond valence sum calculations indicate that the valence of Co is +2. So the cobalt atoms are reduced from Co^{3+} to Co^{2+} in the reaction.

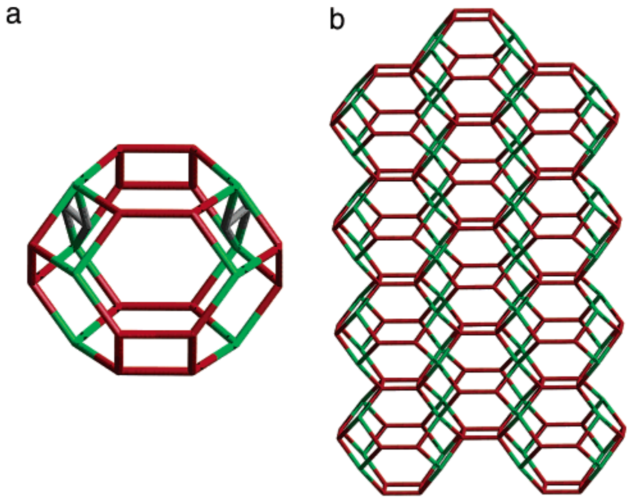

Figure 2. (a) Distorted β cage unit in the compound. Key: red, vanadium; green, cobalt; ashy, carbon. (b) The framework structure of the compound, viewed along the (100) direction, showing the array of the β cage units (without the $C_2O_4^{2-}$). Key: red, vanadium; green, cobalt.

The sodalite cage, i.e., β cage, is the structural building unit of commercially important zeolites A, X, and Y, which have been extensively studied because of their applications in the fields of catalysis, detergents, etc.[23] So how one can

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create the sodalite-type cage structure is important from both industrial and academic points of view. The classical sodalite-type structures are cubic. It is interesting in application as well as in topology to synthesize noncubic structures because they are usually related to some synthesis mechanism or fundamental structural features.[28] Recently, some compounds with sodalite-type structures have been reported,[11,29−32] in which some structural symmetry is reduced from cubic to low symmetry. Stucky et al. consider that the symmetry reduction of sodalite-type structures in GaGe−SOD2 is due to the ordering of the organic structure directing agents and the strong host−guest hydrogen bonding between terminal NH_3^+ groups and framework oxygen atoms.[29] In the title compound, besides the hydrogen bonding between terminal NH_3^+ groups and framework oxygen atoms, one of the primary units is CoO_6 octahedra instead of CoO_4 tetrahedrons which is common in phosphate molecular sieves. Furthermore, C_2O_4 groups are coordinated with two cobalt atoms and located in the 6-ring windows (Figure 2b), so this inorganic/organic hybrid framework compound exhibits orthorhombic symmetry instead of cubic although its structure consists of sodalite cages.

The structure of the compound can also be envisioned as being built up from two kinds of simple building units. One basic building unit of tetranuclear $\{V_4O_{12}\}$, shown in Figure 3a, is a four-membered ring formed only by tetrahedral VO_4 units with corner-sharing. This $\{V_4O_{12}\}$ unit in the μ_4 mode was also found in $[\{Co(3,3'\text{-bpy})_2\}_2V_4O_{12}]$, $[Zn_2(tp)(4,4'\text{-bpy})V_2O_6]$, and so on.[33−35] Another basic building unit of dinuclear $\{Co_2(C_2O_4)O_8\}$, shown in Figure 3b, is a dinuclear oxide oxalate. The two cobalt atoms show the same coordination state, a CoO_6 octahedron. The two kinds of basic building units are connected with each other via oxygens in an alternative manner, to form a three-dimensional architecture with four-membered- and six-membered-ring channels (Figure 4.). In this structure, a $\{V_4O_{12}\}$ unit connects six $\{Co_2(C_2O_4)O_8\}$ dimers, and a $\{Co_2(C_2O_4)O_8\}$ unit connected with six $\{V_4O_{12}\}$ tetramers.

Characterization. The powder XRD pattern of the compound is in good agreement with that simulated on the basis of the single-crystal structure.[36] The diffraction peaks on both patterns correspond well in position, suggesting that the as-synthesized sample is pure. The difference in reflection intensity between the simulated and experimental patterns is due to a certain degree of preferred orientation of the powder sample during data collection.

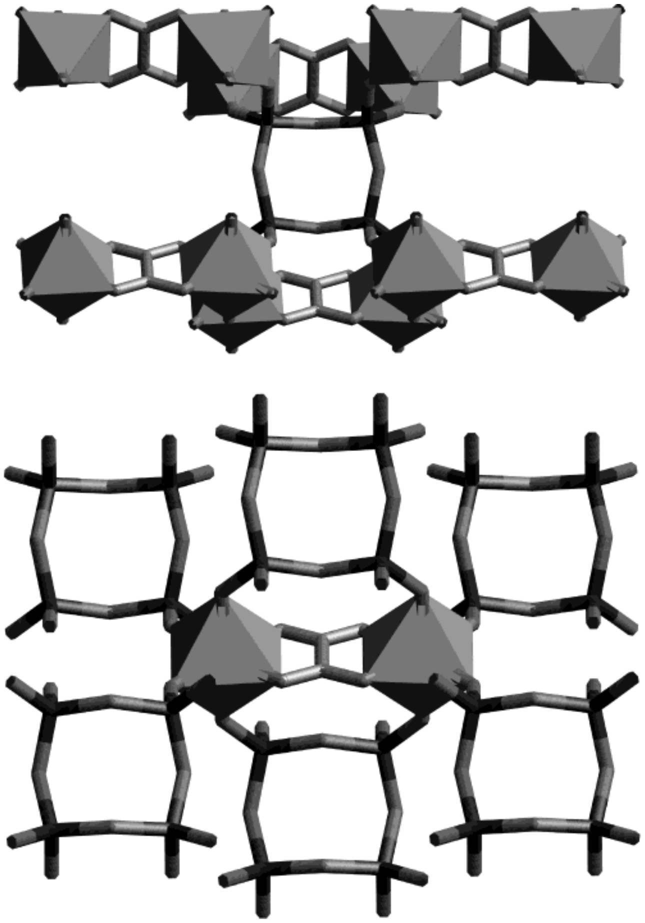

Figure 3. (a) The basic building unit of tetranuclear $\{V_4O_{12}\}$. (b) The basic building unit of dinuclear $\{Co_2(C_2O_4)O_8\}$.

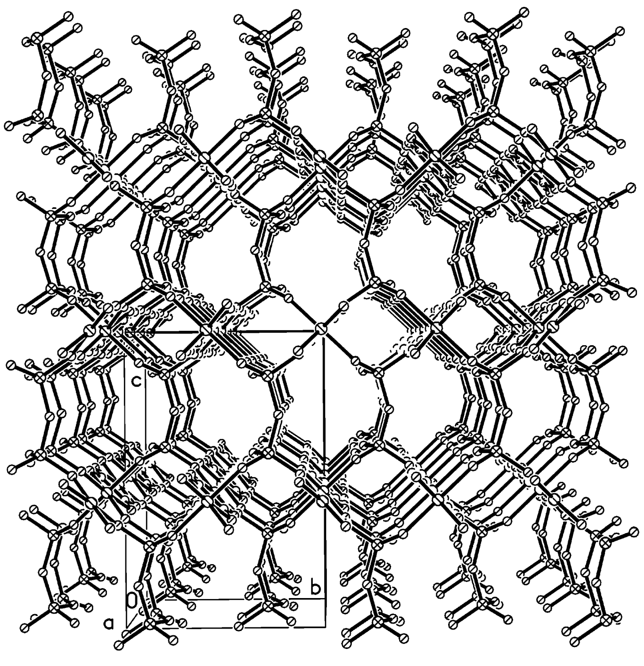

Figure 4. Projection of the framework along the (100) direction showing the 4-ring and 6-ring channels in the compound.

The IR spectra of the compound show vibration modes for V−O, C−O, C−N, C−H, and N−H. The strong bands at 422, 466, 488 cm $^{-1}$ are assigned to the V−O stretching vibrations. The bonds in the range 980−1320 cm^{-1} are

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attributed to the C−O and C−N stretching vibrations, the bonds at 1540 and 1627 cm^{-1} are assigned to the N−H and C−H bending vibrations, and the bonds at 2853, 2918, and 2979 cm^{-1} are assigned to the C−H stretching vibrations. Those at 3310 and 3438 cm^{-1} are assigned to N−H stretching vibrations.

The TG and DTA curves which were recorded in air show that the initial weight loss in the range 300−390 °C is due to the decomposition of ethylenediamine and oxalate (weight loss exptl 23.7%, calcd 22.6%). In addition, the DTA curve shows that an endothermic effect occurs at ca. 760 °C, but the TG curve does not show weight loss at the same temperature. This may be due to a phase transformation. To analyze the sample heated by powder X-ray diffraction, the compound was heated at 800 °C for 4 h and then cooled to room temperature. The powder diffraction pattern shows that the compound transformed to a solid solution at 800 °C. The TG and DTA curves which were recorded in nitrogen gas show similar information. The DTA curve recorded in nitrogen gas shows that three endothermic effects occurred at ca. 760 °C, ca. 835 °C, and ca. 870 °C, probably due to phase transformations. To the DTA curve recorded in air this is the only difference.

To identify the thermodynamical stability of the inorganic framework, the compound was heated at 400 °C for 4 h and then cooled to room temperature. The sample heated was analyzed by powder X-ray diffraction. The powder diffraction pattern shows that the framework of the compound is unstable upon the thermal decomposition of the enH_2^{2+} and $C_2O_4^{2-}$, and it becomes amorphous when the enH_2^{2+} and $C_2O_4^{2-}$ are removed from the structure.

Conclusions

The novel microporous material with sodalite analogue structure, $(C_2H_{10}N_2)[Co_2(C_2O_4)V_4O_{12}]$, has been synthesized and characterized. The compound provides a novel example of an inorganic/organic hybrid framework built by tetrahedral VO_4, CoO_6 octahedra, and C_2O_4 groups. It is noteworthy that we can make new novel structure by basic building units.

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Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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