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# Hydrothermal synthesis and crystal structure of a layered vanadium oxide with an interlayer metal co-ordination complex: $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$

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The compound $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$ was synthesized from the hydrothermal reactions of $V_2O_5$, $CdSO_4$, 1,2-diaminopropane (enMe) and water in the molar ratio 1 : 1 : 2.2 : 223. Its structure has been determined by single-crystal X-ray diffraction. This compound has an open three-dimensional framework structure consisting of $[V_8O_{20}]^{4-}$ layers, composed of equal numbers of $VO_4$ tetrahedra and $VO_5$ pyramids connected by both corner and edge sharing. The $Cd[enMeH]_2^{4+}$ complex occupies the interlayer space and connects with the vanadium oxide layers through four Cd–O bonds. This arrangement gives one-dimensional channels with 10-membered rings along the *c* axis.

## Introduction

There is significant interest in the designed synthesis of solid-state materials consisting of alternative organic and inorganic components, especially transition metal oxides, which have practical applications in areas of catalysis, sorption, molecular electronics and photochemistry.[1–4] In studies of those materials, a series of novel structures with one-, two- and three-dimensions (1-D, 2-D and 3-D)[5–13] have been prepared by using polar organic molecules as structural directors of crystallization of inorganic frameworks. Studies on layered inorganic oxides or metal–oxygen clusters have been well developed. These layered oxides, containing transition and post transition metals, share a common structural feature, acting as "host" materials, and organic amines or cationic guests are accommodated between the anionic oxide layers.[14–18] Especially the mixed-valence vanadium oxides intercalated with organic molecules or polymers such as $[H_3N(CH_2)_3NH_3][V_4O_{10}]$[19,20] and $[C_6H_{14}N_2][V_6O_{14}]\cdot H_2O$[21,22] show a variety of novel frameworks and mixed valence characters. These layer structures are mainly composed by edge- and corner-sharing vanadium oxygen atom square pyramids (or distorted octahedra) and tetrahedra. Different orientations of the different polyhedra led to variations in the layered structure. Recently, several studies have been reported on the hydrothermal synthesis of layered mixed-valence vanadium oxides such as $[Zn(bpy)_2]_2[V_7O_{17}]$, $[Zn(en)_2][V_6O_{14}]$ and $[N(CH_3)_4]_2[Co(H_2O)_4V_{12}O_{28}]$,[23,24] in which interlayer transition and post transition metals co-ordinated with organic ligands and oxygen atoms in the layers lead to a 3-D open framework. Here, we report the synthesis and crystal structure of the novel layered vanadium oxide $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$.

## Experimental

### Synthesis

The compound $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$ was hydrothermally synthesized under autogenous pressure. The starting materials $V_2O_5$ (0.909 g), $CdSO_4$ (1.282 g) and 1,2-diaminopropane (enMe) (0.815 g) were dissolved in 20 ml deionized water in a molar ratio 1 : 1 : 2.2 : 223 to form a solution, which was stirred for 2 h. The solution was sealed in a 30 ml Teflon-lined stainless steel autoclave and heated at 160 °C for 3 d. Black crystalline products were filtered off, washed with distilled water and dried at room temperature. The elemental analyses were performed on a Perkin-Elmer 2400 element analyzer and inductively coupled plasma (ICP) analysis on a Perkin-Elmer Optima 3300DV ICP spectrometer. The ICP analysis showed that the compound contained 41.57% V and 11.85% Cd. The elemental analysis found: C, 7.29; H, 2.15; N, 5.55 (calculated: C, 7.28; H, 2.24; N, 5.66%) corresponding to a molar ratio of C : H : N = 3.06 : 10.75 : 2.0.

Powder X-ray diffraction (XRD) data were obtained using a Siemens D5005 diffractometer with Cu-Kα radiation ($\lambda$ = 1.5418 Å). The IR spectra were recorded on a Nicolet Impact 410 FTIR spectrometer. The TGA-DTA analysis was carried out in air on a Perkin-Elmer DTA 1700 differential thermal analyzer.

### Crystallography

The crystallographic data for $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$ (size 0.44 × 0.32 × 0.30 mm) were collected on a Siemens R3m diffractometer using the $\omega$-scan technique with graphite monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å). The data were corrected for Lorentz-polarization effects, and absorption corrections were applied.[25] All of the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were generated geometrically and allowed to ride on their parent carbon or nitrogen atoms. Atoms C2 and C3 of 1,2-diaminopropane occupy two disordered positions, and each has 0.5 occupancy. Only one conformation of the disordered group is shown in Fig. 1. Further details of the X-ray structural analysis are given in Table 1. Selected bond lengths and angles are listed in Table 2. Drawings were produced with SHELXTL PC.[26]

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See http://www.rsc.org/suppdata/dt/a9/a908773g/ for crystallographic files in .cif format.

## Results and discussion

Hydrothermal synthesis is a useful technique to prepare porous crystals, complex oxides electrolytes and complex fluorides.[27–29]

**Table 1** Crystal data and structure refinement for $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$

| | |
|---|---|
| Empirical formula | $C_3H_{11}Cd_{0.50}N_2O_{10}V_4$ |
| Formula weight | 495.10 |
| $T$/K | 295(2) |
| Crystal system | Monoclinic |
| Space group | $C2/m$ |
| $a$/Å | 13.085(8) |
| $b$/Å | 15.847(4) |
| $c$/Å | 6.161(2) |
| $\beta$/° | 102.07(10) |
| $V$/Å$^3$ | 1249.3(9) |
| $Z$ | 4 |
| $\mu$/mm$^{-1}$ | 3.777 |
| Reflections collected | 1630 |
| Independent reflection | 1567 [$R$(int) = 0.0352] |
| Final $R1$, $wR2$ indices [$I > 2\sigma(I)$] | 0.0358, 0.0907 |
| (all data) | 0.0400, 0.0930 |

**Table 2** Selected bond lengths (Å) and angles (°) for $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$

| | | | |
|---|---|---|---|
| Cd(1)–O($1^1$) | 2.234(3) | V(1)–O($2^4$) | 1.997(3) |
| Cd(1)–O(1) | 2.234(3) | V(2)–O(1) | 1.642(3) |
| Cd(1)–O($1^2$) | 2.234(3) | V(2)–O($3^3$) | 1.645(3) |
| Cd(1)–O($1^3$) | 2.234(3) | V(2)–O($4^5$) | 1.676(3) |
| Cd(1)–N($1^1$) | 2.332(5) | V(2)–O(2) | 1.799(3) |
| Cd(1)–N(1) | 2.332(5) | N(1)–C(1) | 1.399(9) |
| V(1)–O(5) | 1.590(3) | N(2)–C(2) | 1.428(9) |
| V(1)–O(4) | 1.900(3) | C(1)–C(2) | 1.457(10) |
| V(1)–O(2) | 1.929(3) | C(2)–C(3) | 1.422(10) |
| V(1)–O(3) | 1.929(3) | | |
| O($1^1$)–Cd(1)–O(1) | 180.0 | O(4)–V(1)–O($2^4$) | 87.89(13) |
| O($1^1$)–Cd(1)–O($1^2$) | 96.32(15) | O(2)–V(1)–O($2^4$) | 77.03(13) |
| O(1)–Cd(1)–O($1^2$) | 83.68(15) | O(3)–V(1)–O($2^4$) | 154.16(14) |
| O($1^1$)–Cd(1)–O($1^3$) | 83.68(15) | O(1)–V(2)–O($3^3$) | 110.14(17) |
| O(1)–Cd(1)–O($1^3$) | 96.32(15) | O(1)–V(2)–O($4^4$) | 106.37(16) |
| O($1^1$)–Cd(1)–N(1) | 93.39(14) | O($3^3$)–V(2)–O($4^4$) | 112.07(16) |
| O(1)–Cd(1)–N(1) | 86.61(14) | O(1)–V(2)–O(2) | 109.11(15) |
| O($1^2$)–Cd(1)–N(1) | 86.61(14) | O($3^3$)–V(2)–O(2) | 111.15(16) |
| O($1^3$)–Cd(1)–N(1) | 93.39(14) | O($4^5$)–V(2)–O(2) | 107.84(14) |
| N($1^1$)–Cd(1)–N(1) | 180.0 | V(2)–O(1)–Cd(1) | 140.53(17) |
| O(5)–V(1)–O(4) | 112.85(16) | V(2)–O(2)–V(1) | 129.66(15) |
| O(5)–V(1)–O(2) | 113.40(15) | V(2)–O(2)–V($1^4$) | 121.28(14) |
| O(4)–V(1)–O(2) | 133.37(13) | V(1)–O(2)–V($1^4$) | 102.97(13) |
| O(5)–V(1)–O(3) | 103.23(17) | V($2^3$)–O(3)–V(1) | 169.0(2) |
| O(4)–V(1)–O(3) | 86.46(14) | V($2^6$)–O(4)–V(1) | 144.4(2) |
| O(2)–V(1)–O(3) | 88.73(13) | C(1)–N(1)–Cd(1) | 120.6(4) |
| O(5)–V(1)–O($2^4$) | 102.20(14) | | |

Symmetry transformations used to generate equivalent atoms: 1 $-x, -y, -z$; 2 $x, -y, z$; 3 $-x, y, -z$; 4 $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; 5 $x, y, z + 1$; 6 $x, y, z - 1$.

However, the process is relatively complex. Many factors can affect the reactions such as the type of initial reactants, starting concentration, pH, crystallization temperature and pressure. In the synthesis of $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$ the enMe molecule acts as both an organic ligand and a reductive agent adjusting the pH value of the reaction system. The pH values of the reaction system were controlled at 7.5–8.2 to obtain a pure crystallized product, whereas out of this pH range no product could be obtained. Other organic amines led to different structures. For example, with 1,3-diaminopropane as the organic ligand we obtained a layered mixed-valence vanadium oxide $[H_3N(CH_2)NH_3][V_4O_{10}]$ which was reported previously.[19,20] Even when $CdSO_4$ was added in the starting reaction mixture, no Cd atoms were found in the structure.

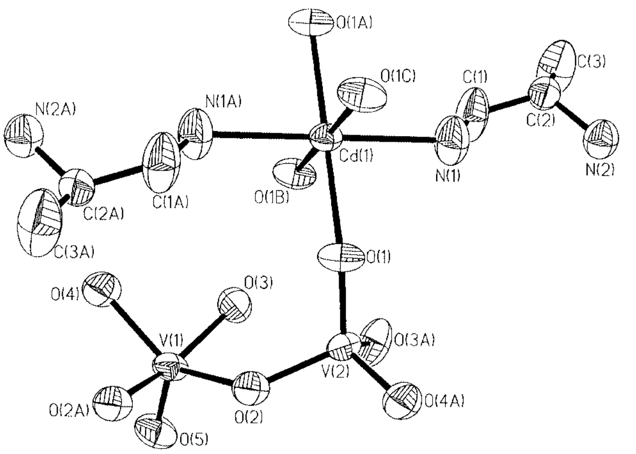

**Fig. 1** The thermal ellipsoid (50% level) plot of $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$ showing the co-ordination environment around the V and Cd and their connections. One conformation of the disordered group of C2 and C3 is shown.

A single crystal structure analysis suggests that $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$ is a novel layered structure containing vanadium oxide layers with $Cd[enMeH]_2^{4+}$ complex occupying the interlayer space. Fig. 1 shows the thermal ellipsoid plot of $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$ and the co-ordination environment around the vanadium and cadmium atom. The V atoms have two different co-ordination environments with oxygen in this structure. The V(1) atom has a distorted square pyramidal configuration with the V–O bond distances ranging from 1.590(3) to 1.997(3) Å and bond angles from 102.20(14) to 113.40(15)°. The V(2) atom is tetrahedrally co-ordinated with four oxygen atoms, and V–O bond distances are in the range 1.642(3) to 1.799(3) Å, bond angles from 106.37(16) to 110.14(17)°. One cadmium atom is octahedrally co-ordinated with four apical oxygen atoms and two N atoms. Each Cd–O bond length is 2.234(3) Å, and the Cd–N bond distance 2.332(5) Å. The N(2), N(2A) atoms of the ligands point toward the oxide layers, forming hydrogen bonds with the terminal oxygen atoms of $VO_5$ from adjacent oxide layers above and below with N···O distances in the range 2.802–2.860 Å.

A view perpendicular to one of the vanadium oxide layers is shown in Fig. 2. The inorganic framework sheets are composed of equal numbers of $VO_4$ tetrahedra and $VO_5$ square pyramids. The $VO_4$ tetrahedra are isolated from each other and the $VO_5$ square pyramids exist in pairs sharing one edge. In each pair of edge-sharing pyramids the two terminal oxygen atoms are oriented toward opposite sides of the plane of the layers. These two different positions are labeled "up" and "down", for the pyramids and the tetrahedra. In rows of tetrahedra the arrangement of tetrahedra is up/up/down/down… In rows of the bipyramidal units the arrangement of the pyramids is alternatively up/down and down/up. Each pair of the pyramids connects with six $VO_4$ tetrahedra *via* corner sharing to form a sheet. Such polyhedral connections have been encountered in the compounds $[H_3N(CH_2)_3NH_3][V_4O_{10}]$ and $[HN(C_2H_4)_3NH][V_6O_{10}]\cdot H_2O$.[21,22]

Fig. 3 shows the framework structure of $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$. The 2-D vanadium oxide layers are interconnected by Cd atoms into a 3-D open framework. This arrangement gives one-dimensional channels with 10-membered rings along the *c* axis. The distance between the vanadium oxide layers is 7.924(4) Å. Bond valence analysis shows that the square pyramids are occupied by $V^{4+}$ ions, and the tetrahedra by $V^{5+}$ ions. This oxidation state is consistent with the overall charge balance of the compound, and confirmed by empirical bond length/valence sum calculations,[30,31] which show a valence of +4.37 for V(1) and +5.35 for V(2). This leads to a mixed valence compound of class I,[32] with localized electrons. The existence of $V^{IV}$ accounts for the black color of the crystal.

The $[V_8O_{20}]^{4-}$ layers in the $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$ are closely related to those found in the structures of $(enH_2)_{0.5}V_2O_5$,[18] $[H_3N(CH_2)NH_3][V_4O_{10}]$[19,20] and $CsV_2O_5$.[33] The layers of those compounds have the same connections of polyhedra. However, the relative orientations of the polyhedra in the present com-

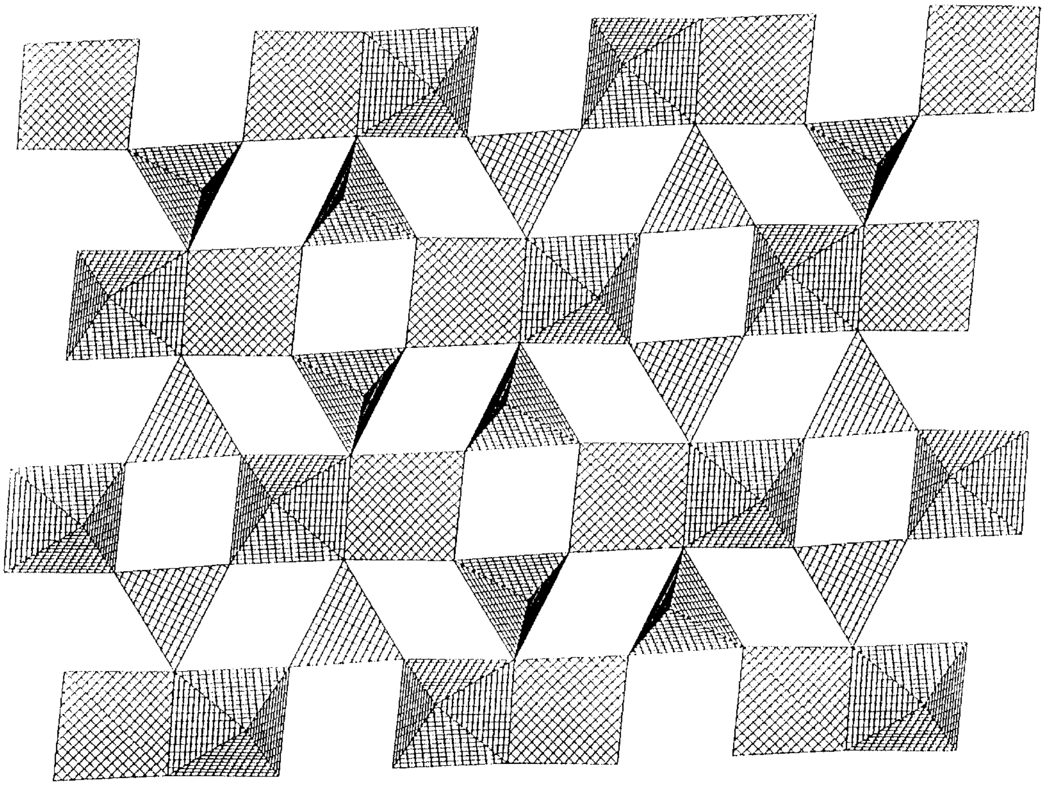

**Fig. 2** Polyhedral representation of the $[V_8O_{20}]^{4-}$ layer along [010] showing the connection of $VO_4$ tetrahedra and $VO_5$ pyramids.

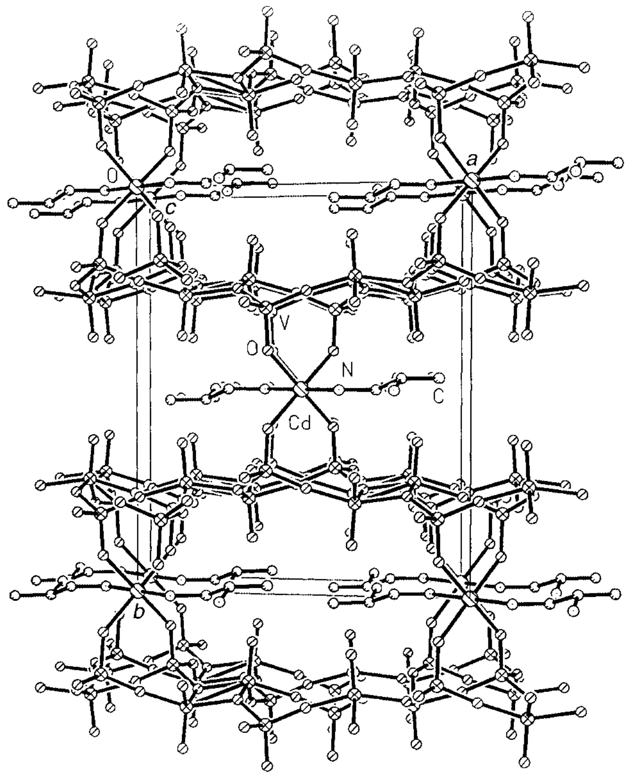

**Fig. 3** View of the framework structure of $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$ showing the vanadium oxide layers connected by Cd into a 3-D framework with 1-D channels.

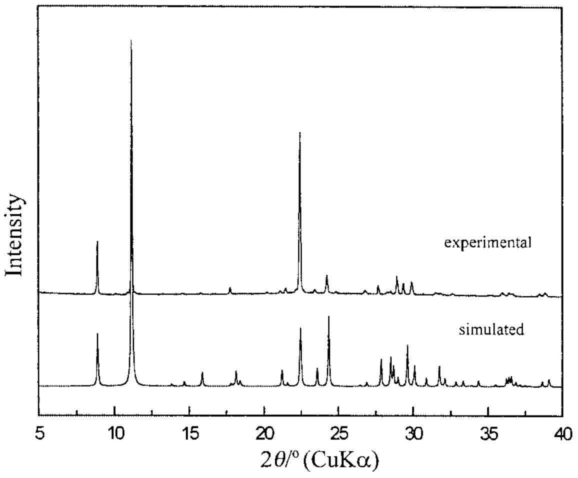

**Fig. 4** Experimental and simulated powder X-ray diffraction pattern of $Cd[C_3N_2H_{11}]_2[V_8O_{20}]$.

pound are different. For example, the tetrahedra in $[H_3N(CH_2)NH_3][V_4O_{10}]$ are arranged up and down alternatively, and the tetrahedra in $CsV_2O_5$ are all up or all down. In our case, every two tetrahedra have the same orientation and are alternatively up and down from one pair of tetrahedra to the other pair. The special polyhedra orientation of the structure may be decided by the interlayer of Cd atoms which connects with four apical oxygen atoms of tetrahedra, and this linkage is relatively strong with a distance of 2.332(5) Å.

The powder XRD pattern of the compound and the pattern simulated on the basis of the single crystal structure is presented in Fig. 4. The diffraction peaks in both patterns correspond well in position, indicating the phase purity of the as-synthesized sample.

In the IR spectrum of the compound the strong bands at 902.5, 979.6, 838.9 and 605.0 cm$^{-1}$ are due to the terminal V=O stretch or a V–O–V stretch. Bands in the 1380.2–1610.3 cm$^{-1}$ region are assigned to C–N stretching, and those at 2927.4 and 2987.6 cm$^{-1}$ to the C–H stretch. Bands in the 3250 to 3470 cm$^{-1}$ region can be attributed to N–H stretching.

In the TGA curves two steps of total weight loss of 15.75% in the range 310–428 °C showed that the enMe molecule was combusted from the crystal. A little weight gain of 1.87% between 430 and 470 °C was shown in the TGA curves, consistent with the oxidation of the $[V_8O_{20}]^{4-}$ framework from $V^{4.5+}$ to $V^{5.0+}$. In

DTA curves there were two exothermic peaks at 310–470 °C, corresponding to the removal of enMe and the oxidation of vanadium in the TGA curves.

In summary, we have successfully introduced a transition metal co-ordination complex into layered oxides to obtain a novel structural framework by the hydrothermal method. This work led from 2-D layered vanadium oxides to a 3-D open framework with 1-D channels and generated a new kind of layer oxides. This work also shows that hydrothermal synthesis is a powerful method in the synthesis of novel structural metal oxides and also provides a good way to obtain inorganic/organic hybrid materials.

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