

$[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3[\text{V}_{15}\text{O}_{36}(\text{Cl})](\text{NH}_3)_6(\text{H}_2\text{O})_3$: Synthesis and Structure Determination of a Novel Centered Tricosahedral Cluster Compound Related to the Müller-Type Structure

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A new microstructured mixed-valence oxovanadate with formula $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3[\text{V}_{15}\text{O}_{36}(\text{Cl})](\text{NH}_3)_6(\text{H}_2\text{O})_3$ has been prepared hydrothermally (443 K, autogeneous pressure) by prolonged heating (5 days) of an aqueous mixture of $\text{NH}_2(\text{CH}_2)_8\text{NH}_2$ and V_2O_5 in acidic HCl (1 M) medium. Its structure was solved by single-crystal X-ray diffraction at two temperatures (293 and 150 K). It is hexagonal (space group $P6_3/mmc$, $Z = 2$) with cell parameters $a = 18.730(3) \text{ \AA}$, $c = 11.040(3) \text{ \AA}$, and $V = 3354.1(5) \text{ \AA}^3$ at 293 K and $a = 18.626(3) \text{ \AA}$, $c = 10.961(3) \text{ \AA}$, and $V = 3293.2(5) \text{ \AA}^3$ at 150 K. Spherical cluster shells, $[\text{V}_{15}\text{O}_{36}]$, built up from the linkage of 15 VO_5 square pyramids, encapsulate the Cl^- anionic species. Six $[\text{V}_{15}\text{O}_{36}(\text{Cl})]^{6-}$ clusters run along the threefold axis to form infinite pseudo-hexagonal one-dimensional channels (diameter 12.84 Å) inside which three $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]^{2+}$ chains are accommodated. Application tests in rechargeable lithium cells are presented. © 1998 Academic Press

Key Words: vanadium oxides; surfactants; mixed valence.

INTRODUCTION

Prompted by the discovery of cubic, hexagonal, and lamellar structures in mesoporous silica (1,2), interest in transition metal oxides possessing a mesoporous structure has increased over the past few years. Recently, amphiphilic molecules have been used as templating agents for mesostructured solids with transition metal oxides. Among these studies, numerous papers have been devoted to vanadium oxides (3–10) or vanadium–phosphorus oxides (11–14). Following these guidelines, we report on the synthesis and structural characterization of a new microstructured vanadium oxide, $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3[\text{V}_{15}\text{O}_{36}(\text{Cl})](\text{NH}_3)_6(\text{H}_2\text{O})_3$, related to the Müller-type structure.

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EXPERIMENTAL

Synthesis

This new structured vanadate compound was prepared by mixing V_2O_5 , 1,8-diaminooctane, HCl (1 M), and H_2O in relative molar ratios of 1:1.5:1.8:239. The starting mixture (pH 2) was placed without stirring into a Teflon-lined stainless steel autoclave, heated at 443 K under an autogeneous pressure for 5 days, and then cooled to room temperature for 15 hr. Black platelike crystals mixed with green powder were obtained in a medium of final pH about 6. The solid was filtered out, washed with water, and air-dried.

A small amount of handpicked crystals was studied by TGA coupled with a mass spectrometer under argon. A first weight loss of 2.5%, attributed to water molecules, was observed between 463 and 493 K, and a second weight loss of 4.8%, attributed to ammonia molecules, was observed between 493 and 523 K. Between 523 and 823 K another weight loss of about 21%, attributed to decomposition of octyldiammonium chains, was observed. The as-obtained residue was amorphous and could not be identified even though the presence of some vanadium suboxide was expected. The results of the analysis gave molecular ratios of $\text{H}_2\text{O}/\text{NH}_3 \approx 0.49$ and $\text{H}_2\text{O}/\text{octyldiammonium} \approx 0.96$.

At this stage we were unable to propose a complete formulation, which was finally established after a complete structural determination.

Structure Determination

Single-crystal intensity data of the structured compound were collected on a STOE imaging plate diffraction system. No absorption correction was applied. The reflection data were averaged to give a set of independent intensities. The structures were solved by a combination of direct methods and Fourier syntheses using the XS and XL routines of the SHELXTL program chain Version 5 (16). The HFIX

subroutine option (riding model) of the SHELXTL programs was retained for positioning and refining hydrogen atoms.

The structure was refined from data collected at two temperatures: 293 and 150 K. The structure refinement was first carried out in the $P6_3/mmc$, space group, one of the possible space groups according to the systematic extinctions. In a first step, vanadium atoms were readily found to form a kind of cage, made up from 15 vanadium atoms, inside which an important electron residue appeared from a difference-series Fourier synthesis. That residue was soon attributed to the Cl⁻ anion. After position parameter refinement and another Fourier synthesis, oxygen atoms of the vanadium coordination appeared together with three more oxygen atoms in a ternary geometry arrangement around the threefold axis, close to the oxovanadium cluster. These three oxygen atoms were subsequently attributed to water

molecules. After further refining, nitrogen atoms belonging to the diaminoctane chains were evidenced together with six other ammonia molecules. Advancing in the resolution of the structure allowed the successive refinement of carbons and hydrogen atoms of the octyldiammonium chain.

At this stage, several other space groups— $P\bar{3}1c$, $P31c$, $P6_3mc$, $P6_322$, and $P\bar{6}2c$ —were checked tentatively to locate the organic chain as precisely as possible. Also, for each group, attempts to replace ammonia molecules between octyldiammonium chains by water molecules did not improve the R factor but rather resulted in a poorer value of R .

Thus, we proposed the formulation [NH₃(CH₂)₈NH₃]₃[V₁₅O₃₆(Cl)](NH₃)₆(H₂O)₃ deduced from crystallography for the new microstructured compound. It should be noted that the theoretical mass percentages for water (2.74%), ammonia (5.19%), octyldiammonium, (22.23%) and

TABLE 1
Crystal Data, Data Collections, and Refinements of [NH₃(CH₂)₈NH₃]₃[V₁₅O₃₆(Cl)](NH₃)₆(H₂O)₃ at 293 and 150 K

Crystal Data		
Chemical formula	[NH ₃ (CH ₂) ₈ NH ₃] ₃ [V ₁₅ O ₃₆ (Cl)](NH ₃) ₆ (H ₂ O) ₃	
Formula mass (amu)	1970.63	
Crystal system	Hexagonal	
Space group	$P6_3/mmc$	
Z	2	
Radiation	MoK α , $\lambda = 0.7107 \text{ \AA}$	
Description	Black platelike crystal	
Size (mm)	0.36 × 0.08 × 0.08	
Temperature (K)	293	150
Unit cell determination	201 reflections	138 reflections
a (Å)	18.730(3)	18.626(3)
b (Å)	18.730(3)	18.626(3)
c (Å)	11.040(3)	10.961(3)
α (deg)	90.0	90.0
β (deg)	90.0	90.0
γ (deg)	120.0	120.0
V (Å ³)	3354.1(5)	3293.2(5)
ρ_{calc} (g cm ⁻³)	1.919	1.987
μ (MoK α) (mm ⁻¹)	2.12	2.16
Data Collection		
Diffractometer type	STOE imaging plate	
θ range (deg)	2.9–48.4	
Index ranges	– 21 ≤ h ≤ 21, – 21 ≤ k ≤ 21, – 11 ≤ l ≤ 11	
Collected reflections	17110	21039
Independent reflections	976 [$R(\text{int}) = 0.0637$]	967 [$R(\text{int}) = 0.0750$]
Observed reflections with $I > 4\sigma(I)$	699	644
Refinement (on F^2)		
Atomic scattering factors	Neutral atoms from SHELXTL software	
No. of variables	89	89
$R_1(F)$	0.0348	0.0515
$wR_2(F^2)$	0.0970	0.1385
Goodness-of-fit on F^2	0.738	0.897
Extinction coefficient	0.0014(1)	0.0014(1)
Largest diff peak and hole ($e \text{ \AA}^{-3}$)	0.298 and – 0.313	0.99 and – 1.19

oxovanadium species (69.8%) are in reasonable agreement with the experimental values deduced from TGA analysis.

From this composition it results that octyldiamine has, for one part, reduced the pentavalent vanadium to form a mixed valence and, for another part, textured the cluster $[V_{15}O_{36}(Cl)]^{6-}$. This double role has already been found

for other diamines and mixed-valence oxides (3, 4, 6–8). An interesting question concerns the presence of ammonia molecules in this compound, since it was not initially introduced in the reaction mixture. Probably, it results from a breakup of the octyldiammonium cations, catalytically assisted by the presence of the mixed-valence vanadium oxide.

TABLE 2

Positional and Thermal Parameters for $[NH_3(CH_2)_8NH_3]_3[V_{15}O_{36}(Cl)](NH_3)_6(H_2O)_3$ Recorded at $T = 293$ K

Atom	Occupancy	x	y	z	$U(eq)^a$ (\AA^2)
V(1)	3	0.5657(1)	0.1314(1)	0.7500	0.0360(4)
V(2)	6	0.4724(1)	0.2362(1)	0.5997(1)	0.0416(4)
V(3)	6	0.6036(1)	0.2072(1)	0.5032(1)	0.0436(4)
Cl	1	0.6667	0.3333	0.7500	0.047(1)
O(1)	6	0.5695(3)	0.2847(2)	0.4734(5)	0.042(1)
O(2)	6	0.3957(3)	0.1979(2)	0.5090(5)	0.055(2)
O(3)	12	0.5158(2)	0.3516(2)	0.6203(3)	0.039(1)
O(4)	6	0.5720(2)	0.1440(3)	0.3917(5)	0.057(2)
O(5)	3	0.4268(4)	0.2134(2)	0.7500	0.041(2)
O(6)	3	0.5160(2)	0.0319(4)	0.7500	0.052(2)
Ow(7)	3	0.4834(4)	0.2417(2)	0.2500	0.054(2)
H(1)	6	0.520(6)	0.260(3)	0.324(9)	0.106
N(1) ^b	6	0.3994(5)	0.3994(5)	0.5000	0.114(3)
N(2)	6	0.4092(5)	0.3389(5)	0.2500	0.091(3)
H(2A)	6	0.4512(4)	0.3732(4)	0.2966(1)	0.137
H(2B)	6	0.4085(4)	0.3651(4)	0.1831(1)	0.137
H(2C)	6	0.4148(4)	0.2959(4)	0.2300(1)	0.137
C(1)	6	0.338(1)	0.312(1)	0.311(2)	0.113(5)
H(1A)	6	0.330(1)	0.358(1)	0.333(2)	0.136
H(1B)	6	0.337(1)	0.283(1)	0.384(2)	0.136
C(2)	6	0.264(1)	0.248(1)	0.289(2)	0.132(7)
H(2A)	6	0.264(1)	0.205(1)	0.320(2)	0.158
H(2B)	6	0.257(1)	0.278(1)	0.356(2)	0.158
C(3)	6	0.195(3)	0.217(2)	0.301(4)	0.276(9)
H(3A)	6	0.194(3)	0.262(2)	0.345(4)	0.332
H(3B)	6	0.196(3)	0.178(2)	0.358(4)	0.332
C(4)	6	0.173(2)	0.054(2)	0.706(4)	0.310(9)
H(4A)	6	0.207(2)	0.078(2)	0.634(4)	0.372
H(4B)	6	0.119(2)	0.011(2)	0.684(4)	0.372

Anisotropic U_{ii} and U_{ij} at 293 K

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V(1)	0.036(1)	0.030(1)	0.040(1)	0	0	0.015(1)
V(2)	0.036(1)	0.041(1)	0.047(1)	-0.004(1)	-0.007(1)	0.018(1)
V(3)	0.048(1)	0.048(1)	0.035(1)	-0.006(1)	-0.003(1)	0.024(1)
Cl(4)	0.047(1)	0.047(1)	0.045(2)	0	0	0.024(1)
O(1)	0.042(2)	0.045(2)	0.038(3)	-0.002(1)	-0.003(2)	0.021(1)
O(2)	0.044(2)	0.064(2)	0.049(3)	-0.006(1)	-0.013(2)	0.022(1)
O(3)	0.038(1)	0.041(1)	0.038(2)	0.001(1)	-0.003(1)	0.019(1)
O(4)	0.065(2)	0.066(3)	0.041(3)	-0.019(2)	-0.009(1)	0.033(1)
O(5)	0.039(3)	0.042(2)	0.041(4)	0	0	0.020(1)
O(6)	0.048(2)	0.030(3)	0.072(5)	0	0	0.015(1)
Ow(7)	0.055(4)	0.060(3)	0.045(4)	0	0	0.028(2)
N(1) ^b	0.124(5)	0.124(5)	0.111(8)	-0.002(2)	0.002(2)	0.080(6)
N(2)	0.077(4)	0.069(4)	0.131(7)	0	0	0.041(4)

$$^a U(eq) = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

^b Ammonia molecules.

TABLE 3

Positional and Thermal Parameters for $[NH_3(CH_2)_8NH_3]_3[V_{15}O_{36}(Cl)](NH_3)_6(H_2O)_3$ Recorded at $T = 150$ K

Atom	Occupancy	x	y	z	$U(eq)^a$ (\AA^2)
V(1)	3	0.5649(1)	0.1299(1)	0.7500	0.0281(6)
V(2)	6	0.4723(1)	0.2361(1)	0.5986(2)	0.0293(5)
V(3)	6	0.6032(1)	0.2064(1)	0.5024(2)	0.0401(5)
Cl	1	0.6667	0.3333	0.7500	0.032(1)
O(1)	6	0.5691(4)	0.2846(2)	0.4724(8)	0.032(2)
O(2)	6	0.3942(3)	0.1971(2)	0.5078(6)	0.036(2)
O(3)	12	0.5149(2)	0.3520(2)	0.6202(4)	0.031(1)
O(4)	6	0.5715(2)	0.1430(4)	0.3892(7)	0.054(2)
O(5)	3	0.4275(4)	0.2137(2)	0.7500	0.029(2)
O(6)	3	0.5152(2)	0.0304(5)	0.7500	0.040(2)
Ow(7)	3	0.4839(5)	0.2420(3)	0.2500	0.042(2)
H(1)	6	0.527(9)	0.263(5)	0.31(2)	0.22
N(1) ^b	6	0.3968(6)	0.3968(6)	0.5000	0.086(4)
N(2)	6	0.4093(6)	0.3389(5)	0.2500	0.060(3)
H(2A)	6	0.4521(5)	0.3731(5)	0.2962	0.0904
H(2B)	6	0.4080(5)	0.3655(5)	0.1833	0.0904
H(2C)	6	0.4144(5)	0.2956(5)	0.2287	0.0904
C(1)	6	0.337(1)	0.312(1)	0.314(2)	0.081(5)
H(1A)	6	0.330(1)	0.358(1)	0.338(2)	0.095
H(1B)	6	0.337(1)	0.283(1)	0.387(2)	0.095
C(2)	6	0.259(1)	0.247(1)	0.285(3)	0.111(8)
H(2A)	6	0.267(1)	0.202(1)	0.314(2)	0.119
H(2B)	6	0.252(1)	0.276(1)	0.352(3)	0.119
C(3)	6	0.192(3)	0.218(3)	0.310(5)	0.25(2)
H(3A)	6	0.189(3)	0.264(3)	0.345(5)	0.287
H(3B)	6	0.194(3)	0.181(3)	0.368(5)	0.287
C(4)	6	0.168(2)	0.053(3)	0.709(5)	0.28(3)
H(4A)	6	0.198(2)	0.078(3)	0.635(5)	0.316
H(4B)	6	0.113(2)	0.009(3)	0.691(5)	0.316

Anisotropic U_{ii} and U_{ij} at 150 K

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V(1)	0.020(1)	0.016(1)	0.047(2)	0	0	0.008(1)
V(2)	0.020(1)	0.024(1)	0.043(1)	-0.001(1)	-0.003(1)	0.010(1)
V(3)	0.039(1)	0.041(1)	0.041(1)	-0.008(1)	-0.004(1)	0.021(1)
Cl	0.026(1)	0.026(1)	0.044(4)	0.00	0.00	0.013(1)
O(1)	0.021(2)	0.027(2)	0.039(5)	0.000(1)	0.03(4)	0.011(2)
O(2)	0.028(3)	0.038(2)	0.041(4)	-0.003(1)	-0.006(3)	0.014(1)
O(3)	0.022(2)	0.026(2)	0.043(3)	0.000(2)	-0.005(2)	0.011(2)
O(4)	0.052(3)	0.062(4)	0.051(5)	-0.013(4)	-0.006(2)	0.031(2)
O(5)	0.026(4)	0.022(3)	0.040(6)	0	0	0.013(2)
O(6)	0.028(3)	0.020(4)	0.069(7)	0	0	0.010(2)
Ow(7)	0.033(5)	0.030(3)	0.066(8)	0	0	0.017(2)
N(1) ^b	0.086(6)	0.086(6)	0.100(10)	-0.003(3)	0.003(3)	0.053(6)
N(2)	0.050(5)	0.048(5)	0.092(8)	0.00	0.00	0.031(4)

$$^a U(eq) = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$$

^b Ammonia molecules.

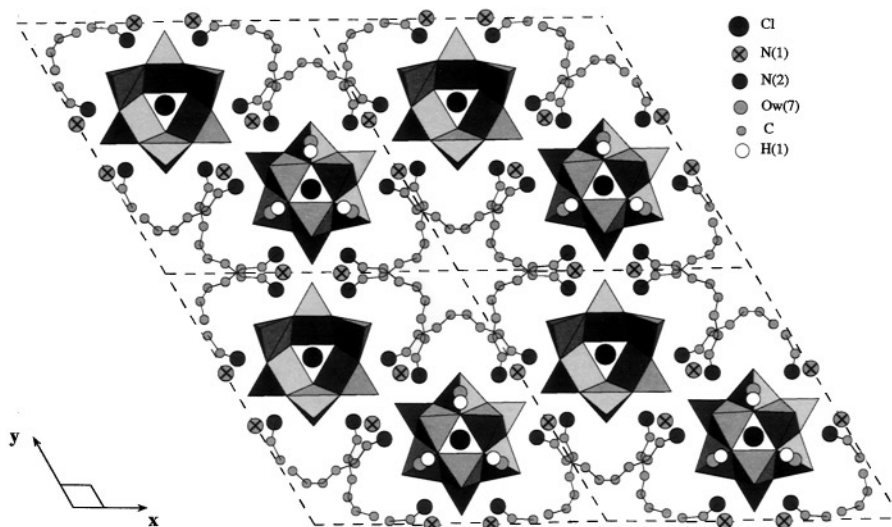


FIG. 1. Crystal structure of [NH₃(CH₂)₈NH₃]₃[V₁₅O₃₆(Cl)](NH₃)₆(H₂O)₃, showing the six [V₁₅O₃₆(Cl)]⁶⁻ clusters running along the threefold axis to form infinite one-dimensional tunnels in which the octyldiammonium chains are inserted.

Details of the crystal data, data collection, and structure refinement for [NH₃(CH₂)₈NH₃]₃[V₁₅O₃₆(Cl)](NH₃)₆(H₂O)₃ at both 293 and 150 K are given in Table 1. The final atomic coordinates and thermal parameters at 293 and 150 K are reported in Tables 2 and 3, respectively. All atoms except carbon and hydrogen were anisotropically refined.

DESCRIPTION OF THE CRYSTAL STRUCTURE

As shown in Fig. 1, [NH₃(CH₂)₈NH₃]₃[V₁₅O₃₆(Cl)](NH₃)₆(H₂O)₃ can be described as a microstructured² pseudo-hexagonal compound. The six [V₁₅O₃₆(Cl)]⁶⁻ clusters run along the threefold axis to form infinite one-dimensional tunnels in which octyldiammonium chains are inserted (Fig. 1). The diameter of the pseudo-hexagonal “pores” is 12.84 Å, as measured from the O3 positions belonging to adjacent clusters. The building cluster [V₁₅O₃₆(Cl)]⁶⁻ of the [NH₃(CH₂)₈NH₃]₃[V₁₅O₃₆(Cl)](NH₃)₆(H₂O)₃ structure is negatively charged and the [NH₃(CH₂)₈NH₃]²⁺ diamine template is doubly protonated to counterbalance the negative charge.

A [V₁₅O₃₆(Cl)]⁶⁻ unit consists of a spherical oxovanadium shell in which the apical oxygens of the VO₅ square pyramids (Table 4) point out of the cage (Fig. 2). This cluster is closely related to those described by Müller in various structures found in alkali–vanadium oxide–halide

systems, which are extremely rich in phases containing vanadium oxide cluster anions (18,19). Müller *et al.* reported a series of water-soluble vanadium oxides with such cavities in which anions (chloride, bromide, iodide, and carbonate) are encapsulated. Each cluster is built up from a shell of 15 VO₄ square pyramids which encapsulate the Cl⁻ anionic species. The 15 vanadium atoms are arranged on the surface of a sphere at a distance of 3.45 ± 0.15 Å from the center of the cluster, occupied by the Cl⁻ ion. In this compound, the reduced metal cations (V^{IV}) are antiferromagnetically coupled (19), whereby some V^{IV} centers in the mixed-valence V₁₅ species are localized, as shown by the values of the valence bond sums (Table 5). Bond valence calculations using the empirical Brown formula, give a good estimation of the V oxidation state (20). Therefore the detailed formula of the cluster can formally be described as [V₇^VV₈^{IV}O₃₆(Cl)]⁶⁻.

Another reported compound with formula (NH₄)₃Na₇[V₁₅O₃₆(Cl)]·30H₂O according to the literature and refined in the *P*6̄2*m* space group (21) exhibits the charge distribution [V₃^VV₁₂^{IV}O₃₆(Cl)]¹⁰⁻ inside the cluster. Thus, this type of cluster seems to exhibit a large range of mixed valence for the vanadium.

The vanadium oxide cluster constitutes hollow spheres built up from linked VO₅ square pyramids. In these VO₅ both V^{IV} and V^V species are practically located at the center of a square. As shown in Fig. 3, one chloride anion adopts a tricosahedral coordination, implying 23 oxygen atoms (denoted (3⁸4¹⁵)), with the shortest Cl–O distance 3.3342 Å, from oxygen atoms of the basal plane of the square pyramids.

According to the ternary symmetry, the octyldiammonium chains are arranged around the *c* axis (Fig. 4a).

²The terms microstructured, mesostructured, and macrostructured are used analogously to scale definitions for the three classes of porous materials defined by IUPAC (17): first, microporous materials, in which the pore diameter *d_p* < 20 Å; second, mesoporous materials, in which 20 Å < *d_p* < 500 Å; and, third, macroporous materials, in which *d_p* > 500 Å.

TABLE 4
Selected Bond Lengths (Å) and Angles (Deg) in
[NH₃(CH₂)₈NH₃]₃[V₁₅O₃₆(Cl)](NH₃)₆(H₂O)₃

	293 K	150 K
V(1)–O(6)	1.613(5)	1.605(7)
V(1)–O(3) (4 ×)	1.969(3)	1.961(4)
V(1)–V(3)	2.9896(13)	2.982(2)
V(2)–O(2)	1.596(4)	1.605(6)
V(2)–O(5)	1.817(2)	1.810(3)
V(2)–O(3) (2 ×)	1.905(2)	1.905(3)
V(2)–O(1)	2.104(4)	2.084(5)
V(2)–V(3) (2 ×)	2.9676(9)	2.9522(12)
V(3)–O(4)	1.600(4)	1.609(7)
V(3)–O(1) (2 ×)	1.886(2)	1.886(2)
V(3)–O(3) (2 ×)	1.923(3)	1.923(4)
N(2)–C(1)	1.35(2)	1.37(2)
C(2)–C(3)	1.50(4)	1.48(4)
C(1)–C(2)	1.71(2)	1.73(2)
C(4)–C(4)	1.57(9)	1.43(9)
C(3)–C(4)	1.62(4)	1.65(5)
O(6)–V(1)–O(3)	105.70(8)	105.74(11)
O(3)–V(1)–O(3)	93.3(2)	93.0(2)
O(3)–V(1)–O(3)	148.6(2)	148.5(2)
O(3)–V(1)–O(3)	78.2(2)	78.5(2)
O(2)–V(2)–O(5)	104.8(2)	104.8(3)
O(2)–V(2)–O(3)	111.29(8)	111.08(12)
O(5)–V(2)–O(3)	92.39(11)	91.7(2)
O(3)–V(2)–O(3)	134.2(2)	135.2(2)
O(2)–V(2)–O(1)	99.6(2)	100.1(3)
O(5)–V(2)–O(1)	155.6(2)	155.1(3)
O(3)–V(2)–O(1)	78.59(9)	79.2(2)
O(4)–V(3)–O(1)	106.9(2)	106.8(2)
O(1)–V(3)–O(1)	92.8(2)	92.8(3)
O(4)–V(3)–O(3)	106.9(2)	106.6(2)
O(1)–V(3)–O(3)	83.7(2)	83.9(2)
O(1)–V(3)–O(3)	145.7(2)	145.9(2)
O(4)–V(3)–O(3)	106.6(2)	106.6(2)
O(3)–V(3)–O(3)	80.4(2)	80.3(2)
C(2)–C(1)–N(2)	104.1(12)	105.1(14)
C(4)–C(4)–C(3)	95(4)	93(4)
C(2)–C(3)–C(4)	97(3)	97(3)

Each carbon chain is statistically distributed on both sides of a pseudomirror plane in such a way that the zigzag C–C bonds alternate (Fig. 4b). To differentiate the two statistically distributed alkyldiammonium chains, X-ray diffraction data were collected at low temperature (150 K). In the absence of superstructure spots along the *c* axis, data analysis was carried out in the same *P6₃/mmc* space group. Attempts in other subgroups were unsuccessful. As shown Table 6, which reports the carbon–carbon distances between two equivalent atoms on opposite sides of the pseudomirror plane, the distortion amplitude is increasing at lower temperature. With the exception of C(4) atoms, the carbon–carbon bond lengths are not appreciably affected by the distortion (Table 4) but carbon atoms move in such

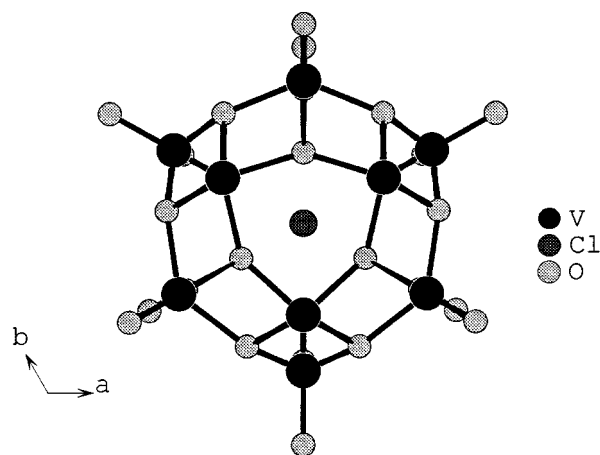


FIG. 2. Arrangement of the discrete Cl-centered tricapped octahedra in the unit cell of [NH₃(CH₂)₈NH₃]₃[V₁₅O₃₆(Cl)](NH₃)₆(H₂O)₃.

a way that the two zigzag chains tend to separate more as temperature is decreased. This thermal differentiation suggests that a structural order–disorder phase transition could be expected at lower temperature. However, no phase transitions were observed from the DSC experiments in the temperature range 110–380 K. Furthermore, it is worth noting that the NH₃(CH₂)₈NH₃ cation lies between the oxovanadium clusters in the [NH₃(CH₂)₈NH₃]₃[V₁₅O₃₆(Cl)](NH₃)₆(H₂O)₃ structure. The nitrogen–oxygen distances from the [NH₃(CH₂)₈NH₃]²⁺ cations, $d_{N(2)-Ow(7)} = 2.789$ Å, being significantly shorter than $d_{N(1)-O(3)} = 3.045$ Å and $d_{N(1)-O(4)} = 3.233$ Å from the free ammonia molecules, imply that the N(2) nitrogen atoms are weakly hydrogen bonded to the water oxygen Ow(7). Moreover, the Ow(7)–O(1) distance is short ($d_{Ow(7)-O(1)} = 2.818$ Å) and thus the water molecule is hydrogen-bonded to the oxygen (O(1)) common to the three VO₅ square pyramids. In this way the three water molecules connect two adjacent clusters to form infinite files along the *c* axis. Those files are also connected around the threefold axis through

TABLE 5
Sums of the Bond Valences for the V Atoms [NH₃(CH₂)₈NH₃]₃[V₁₅O₃₆(Cl)](NH₃)₆(H₂O)₃

	<i>T</i> = 293 K	<i>T</i> = 150 K
V(1)	4.04	4.15
V(2)	4.49	4.48
V(3)	4.56	4.52

Note. The results refer to the equation $\sum_i (d(V-O_i)/178)^{-5.15}$ (19).

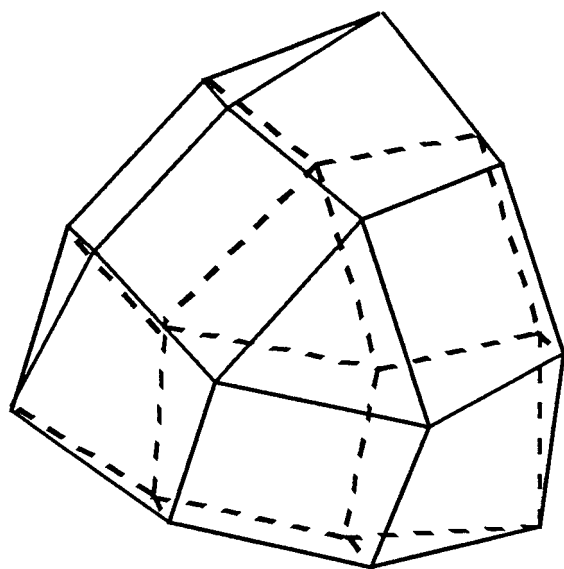


FIG. 3. Tricosahedral oxygen coordination ($3^8 4^{15}$) of the Cl^- anion.

the protons of the ammonium group, which are hydrogen bonded to the water molecule $\text{Ow}(7)$. Ammonia molecules ($\text{N}(1)$) are also stabilized by hydrogen bonding with the hydrogen of the octyl chain, with $d_{\text{N}(1)-\text{C}(1)} = 2.515 \text{ \AA}$.

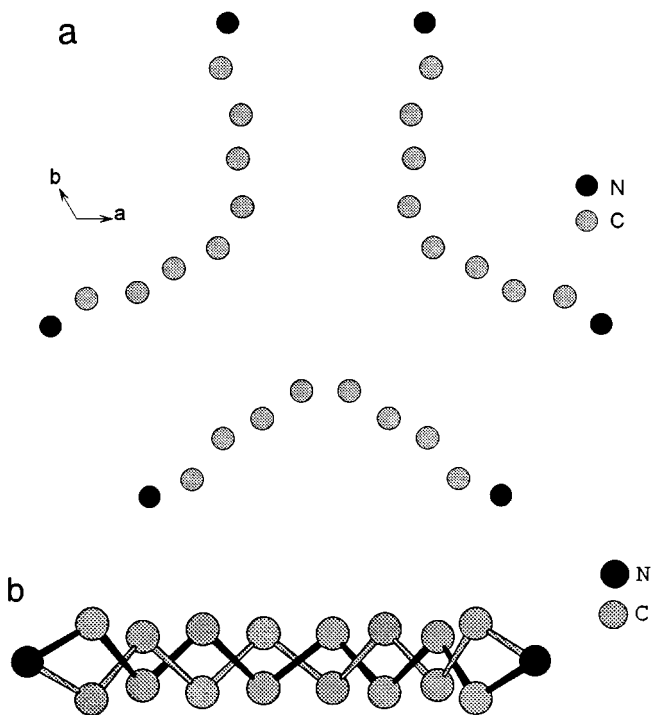


FIG. 4. $\text{NH}_3(\text{CH}_2)_8\text{NH}_3$ chains (a) in projection along the $[001]$ axis and (b) in projection along $[\bar{1}10]$ axis: each alkyl chain is statistically distributed on both sides of a pseudomirror plane in such a way that the zigzag C–C bonds alternate.

TABLE 6
Carbon–Carbon Distances (\AA) between Two Equivalent Atoms on Opposite Sides of the Pseudo Mirror

	$T = 293 \text{ K}$	$T = 150 \text{ K}$
C(1)–C(1)	1.347	1.403
C(2)–C(2)	0.861	0.767
C(3)–C(3)	1.126	1.315
C(4)–C(4)	0.972	0.899

LITHIUM INTERCALATION PROPERTIES

To improve our knowledge of the redox behavior of the new microstructured oxovanadium compound, a few lithium intercalation cycles were carried out. The as-prepared microstructured vanadate was tested with special regard to its potential application as a cathode in rechargeable lithium cells. The composite cathode was prepared by mixing the vanadate, carbon black, and a binder (PVDF) with the relative mass ratios 85:10:5 and then coating the mixture onto an aluminum disk used as a current collector. The standard laboratory Swagelok test cell was used with the composite electrode as the cathode and Li metal as the anode separated with glass paper soaked in the electrolyte (1 M LiPF_6 dissolved in a 2:1 mixture of ethylene carbonate and dimethyl carbonate). The cell was tested using a Mac-Pile system operating through a galvanostatic mode ($10 \mu\text{A}$ between 2 and 4 V/Li).

The first discharge corresponds to intercalation of two Li^+ ions per $[\text{V}_{15}\text{O}_{36}(\text{Cl})]^{6-}$ formula unit in two steps (Fig. 5), the first one at 2.65 V and the second at 2.35 V. Between 3.2 and 2 V, two V^{V} are reduced to V^{IV} when two Li^+ ions (30 mA h g^{-1}) enter the microstructured compound, into or close to the $[\text{V}_{15}\text{O}_{36}(\text{Cl})]$ cluster. Recharging

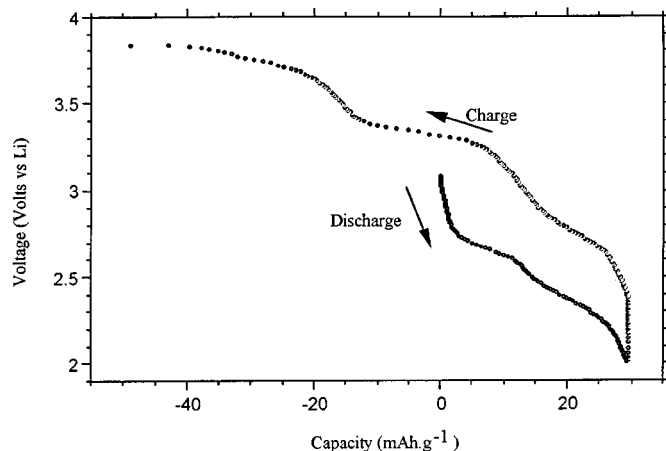


FIG. 5. First discharge and charge for $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3[\text{V}_{15}\text{O}_{36}(\text{Cl})](\text{NH}_3)_6(\text{H}_2\text{O})_3$ in the range 2–4 V.

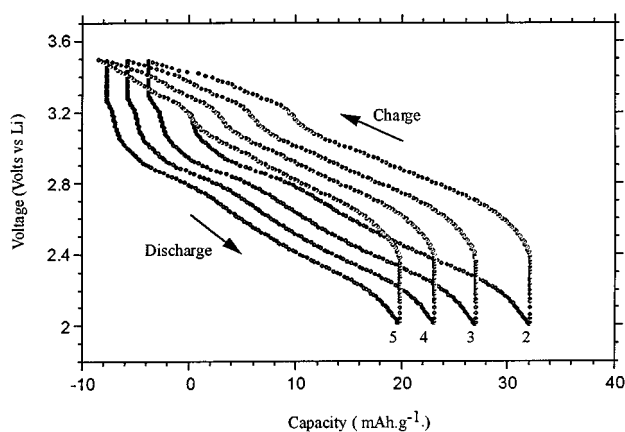


FIG. 6. Further cycling of $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3[\text{V}_{15}\text{O}_{36}(\text{Cl})](\text{NH}_3)_6(\text{H}_2\text{O})_3$ (cycles 2–5) when starting with an initial discharge in the range 2–3.6 V.

the battery allows two Li^+ ions to be deintercalated but at higher potentials. By overcharging, a first plateau is seen on the potential curve about 3.3 V (Fig. 5) and could correspond to oxidation of two V^{IV} to V^{V} by removing most likely two protons from the octyldiammonium groups. At further oxidation, probably important modifications take place in the solid and the solvent is oxidized at a potential of about 3.8 V. After relaxation, lithium intercalation was performed again, between 3.2 and 2 V (Fig. 6). The capacity change between 0 and 32 mA h g^{-1} corresponds again to intercalation of two Li^+ . Lithium deintercalation seems to be almost reversible, the potential values decreasing more and more with number of cycles. The charge–discharge curves are reminiscent of intercalation in metallic compounds where band filling increases on lithium intercalation. Perhaps, even though overcharging induces a weakening of bonding between the octylammonium chain and the $[\text{V}_{15}\text{O}_{36}(\text{Cl})]^{6-}$, the latter remains the effective redox center. In conclusion, it seems easier to intercalate Li^+ , and hence reduce V^{V} , than the reverse. Although preliminary, this study shows that a large mixed-valence range can exist for vanadium in this type of cluster. Further experiments are in progress to verify this point.

CONCLUSION

The new microstructured oxovanadate $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]_3[\text{V}_{15}\text{O}_{36}(\text{Cl})](\text{NH}_3)_6(\text{NH}_3)_6(\text{H}_2\text{O})_3$ is another example illustrating the templating effect of alkyldiammonium chains on $[\text{V}_{15}\text{O}_{36}\text{Cl}]^{6-}$ -type clusters, first described by Müller. These clusters are mixed-valence vanadium oxides that encapsulate different variously charged anions such as Cl^- , Br^- , and CO_3^{2-} . It seems that the $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ distribution is especially stabilized for a ratio 8/7 whatever the counter-cation: lithium, sodium, ammonium, tetramethylammonium, and here the octyldiammonium chain. However, as discussed previously, a compound $(\text{NH}_4)_3\text{Na}_7[\text{V}_{15}\text{O}_{36}(\text{Cl})] \cdot 30\text{H}_2\text{O}$

has been synthesized with a higher value of the $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$ ratio (12/3). The preliminary tests of lithium intercalation in our compound indicate that this cluster type can effectively exhibit a large mixed-valence range for vanadium.

The six $[\text{V}_{15}\text{O}_{36}\text{Cl}]^{6-}$ clusters run along the threefold axis to form infinite pseudohexagonal one-dimensional channels, inside which are accommodated the three $[\text{NH}_3(\text{CH}_2)_8\text{NH}_3]^{2+}$ octyldiammonium chains. These chains are hydrogen bonded to water molecules. Because of the presence of a pseudomirror plane, each alkyl chain is statistically distributed on both sides in such a way that zigzag C–C bonds alternate. The two zigzag chains become more separated as the temperature is decreased, suggesting that a structural order–disorder phase transition could be expected at lower temperature ($T < 110\text{ K}$). Work is currently in progress first to replace the octyldiammonium chains with others of shorter length or with cations and second to encapsulate other differently charged anions.

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