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Chlorovanadates with Original Chain and Layered Structures: $A\mathrm{VO_3Cl}$ (A=Ba, Sr, Cd)

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Three new chlorovanadates, $A\mathrm{VO_3Cl}$ (A=Ba, Sr, Cd), with original structures have been synthesized. They crystallize in the *Pnma* space group with $a = 10.458$ Å, $b = 5.287$ Å, $c = 7.355$ Å, and $a = 10.076$ Å, $b = 5.270$ Å, $c = 6.965$ Å for A = Ba and Sr, respectively, and with $a = 15.647$ Å, $b = 3.662$ Å, $c = 6.837$ Å for A = Cd. The structure of $\mathrm{BaVO_3Cl}$ and $\mathrm{SrVO_3Cl}$ consists of $[\mathrm{BaCl}]_n^{n+}$ or $[\mathrm{SrCl}]_n^{n+}$ chains running along b forming a distorted "honeycomb" lattice whose tubes are occupied by $[\mathrm{VO_3}]_n^{n-}$ chains built up of edge-sharing square pyramids. The $\mathrm{CdVO_3Cl}$ structure can be described as the assemblage of rutile type layers $[\mathrm{Cd_6Cl_6O_7}]_\infty$ interconnected by $[\mathrm{V_6O_{11}}]_\infty$ double chains of edge and corner sharing $\mathrm{VO_5}$ bipyramids. The latter forms five sided tunnels which are empty. © 1999 Academic Press

Vanadium oxides represent a large family of compounds which have been investigated because of their wide applications, especially in the field of catalysis. For these reasons numerous papers about synthesis and crystal chemistry of vanadates (1), vanadium bronzes (2), and vanadium phosphates (3) have been published in the past.

In contrast, very few chlorovanadates have been synthesized to date. Considering the alkaline earth chlorovanadates, only two series of compounds are actually known. The first series, with the formula $A_5(\mathrm{VO_4})_3\mathrm{Cl}$, obtained for A = Ca, Sr, Ba (4), exhibits the apatite structure, whereas the second one corresponds to the formula $A_2\mathrm{VO_4Cl}$ with A = Ca, Sr (5, 6) and exhibits the spodiosite structure. In the present study we have investigated the systems $A\mathrm{O}$–$\mathrm{V_2O_5}$–$A\mathrm{Cl_2}$ for A = Sr, Ba, Cd. We report herein on new chlorovanadates $A\mathrm{VO_3Cl}$ which exhibit original structures. Two of them, $\mathrm{BaVO_3Cl}$ and $\mathrm{SrVO_3Cl}$, exhibit a chain structure, whereas the third one, $\mathrm{CdVO_3Cl}$, has a layered structure built up from distorted rutile slabs interconnected through double pyramidal vanadium chains.

CHEMICAL SYNTHESIS AND CRYSTAL GROWTH

The synthesis of the chlorovanadates $A\mathrm{VO_3Cl}$ was carried out in two steps. First a mixture of $\mathrm{V_2O_5}$ and $A\mathrm{CO_3}$ (A = Sr, Ba, Cd) according to the composition $A\mathrm{V_2O_6}$ was heated up to 973 K in a platinum crucible for 6 hours to liberate $\mathrm{CO_2}$. In the second step $A\mathrm{Cl_2}$ was added to the $A\mathrm{V_2O_6}$ mixture in the 1:1 ratio. After intimate grinding, the resulting mixture was sealed in an evacuated silica ampoule and heated for 24 hours at 753 K and cooled at 8 K per hour down to 573 K and finally quenched down to room temperature. For these experimental conditions polycrystalline yellow samples were obtained whose X-ray powder diffraction patterns were indexed on an orthorhombic cell, in agreement with the single crystal data. In those samples, small yellow needles were isolated. Their investigation, using the Weissenberg technique, allowed the cell parameters to be determined, but the poor quality of these crystals and their small size did not allow their structure determination.

In order to grow single crystals of $A\mathrm{VO_3Cl}$ compounds, lithium chloride was added to the oxides. First, a mixture of $\mathrm{V_2O_5}$ and $A\mathrm{CO_3}$ in the molar ratio 5:3 was heated to 973 K in air in a platinum crucible for decarbonation. The resulting mixture, $A_3\mathrm{V_{10}O_{28}}$, was added with 2 moles of LiCl and heated in a silica ampoule, under the same conditions as those described for the synthesis of polycrystalline samples. From the so-obtained polyphasic samples, yellow single crystals were extracted for the structure determination. The microprobe analysis of these crystals led to an A/Cl/V ratio of 1:1:1 in agreement with the results deduced from the structure determination.

STRUCTURE DETERMINATION

Three yellow single crystals with dimensions $0.116 \times 0.045 \times 0.026$, $0.102 \times 0.051 \times 0.039$, and $0.463 \times 0.013 \times 0.008\ \mathrm{mm^3}$, respectively, for $\mathrm{SrVO_3Cl}$, $\mathrm{BaVO_3Cl}$, and $\mathrm{CdVO_3Cl}$ were selected for the structure determination. The cell parameters were determined by diffractometric techniques at 294 K with a least square refinement based upon 25 reflections with $18 \leq \theta \leq 22°$. The data were collected on a CAD4 ENRAF NONIUS diffractometer with the parameters reported in Table 1. Although the structure of

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TABLE 1
Summary of Crystal Data, Intensity Measurements, and Structure Refinement Parameters for $A\mathrm{VO_3Cl}$

	$\mathrm{BaVO_3Cl}$	$\mathrm{SrVO_3Cl}$	$\mathrm{CdVO_3Cl}$
Crystal data			
Space group	*Pnma*	*Pnma*	*Pnma*
Cell dimensions	$a = 10.4584(9)$ Å $b = 5.2870(4)$ Å $c = 7.3550(4)$ Å	$a = 10.0766(8)$ Å $b = 5.2700(5)$ Å $c = 6.9655(6)$ Å	$a = 15.6473(16)$ Å $b = 3.6621(4)$ Å $c = 6.8376(8)$ Å
Volume $(\text{Å})^3$	406.68(5) Å^3	369.89(6) Å^3	369.89(6) Å^3
Z	4	4	4
dcalc	4.438	3.987	4.184
Intensity measurements			
$\lambda(\mathrm{Mo}K\alpha)$	0.71073	0.71073	0.71073
Scan mode	ω–θ	ω–θ	ω–θ
Scan width (°)	$1 + 0.35 \tan\theta$	$1.05 + 0.35 \tan\theta$	$1.1 + 0.35 \tan\theta$
Slit aperture (mm)	$1 + \tan\theta$	$1.05 + \tan\theta$	$1.1 + \tan\theta$
Max θ (°)	45	45	45
Standard reflections	3 every hour	3 every hour	3 every hour
Measured reflections	1790	1630	1774
Reflections width $I > 3\sigma$	943	533	505
μ (mm^{-1})	12.42	17.49	8.33
Structure solution and refinement			
Parameters refined	35	34	37
Agreement factors	$R = 0.025$ $R_W = 0.028$	$R = 0.033$ $R_W = 0.046$	$R = 0.031$ $R_W = 0.027$
Weighting scheme	$W = 1/\sigma^2$	$W = 1/\sigma^2$	$W = 1/\sigma^2$
Δ/σ max	< 0.0001	< 0.00007	< 0.00004
$\Delta\rho$ $(\mathrm{e\text{Å}^{-3}})$	2.39	2.29	1.23

$\mathrm{CdVO_3Cl}$ is different from those of $\mathrm{SrVO_3Cl}$ and of $\mathrm{BaVO_3Cl}$, the three compounds crystallize in the orthorhombic system, with the same systematic reflection conditions $k + l = 2n$ for $0kl$ and $h = 2n$ for $hk0$, consistent with the space group *Pnma*. The reflections were corrected for Lorentz and polarization effects and absorption (Gaussian method). A secondary extinction correction was made for $\mathrm{BaVO_3Cl}$.

The structures were solved with the heavy atom method. The refinements of the atomic coordinates and of anisotropic thermal factors for all the atoms led to $R = 0.033$ and $R_W = 0.038$, $R = 0.025$ and $R_W = 0.023$, and $R = 0.031$ and $R_W = 0.027$, respectively, for $\mathrm{SrVO_3Cl}$, $\mathrm{BaVO_3Cl}$, and $\mathrm{CdVO_3Cl}$, and to the atomic parameters of Table 2.

The calculations were performed on a SPARK station with XTAL 3.2 programs.

GENERAL FEATURES OF $A\mathrm{VO_3Cl}$ STRUCTURES

The structure of the chlorovanadates $\mathrm{BaVO_3Cl}$ and $\mathrm{SrVO_3Cl}$ consists of an assemblage of $[\mathrm{VO_3}]_n^{n-}$ and $[\mathrm{BaCl}]_n^{n+}$ or $[\mathrm{SrCl}]_n^{n+}$ chains running along **b** as shown from the projections along **b** (Fig. 1a) and along **c** (Fig. 1b). The $[\mathrm{VO_3}]_\infty$ chains are built up of edge-sharing $\mathrm{VO_5}$ pyramids with a trans-configuration (Fig. 1b) whose apical site is free. Such chains have already been observed in the vanadates $A\mathrm{V_3O_7}$ (7) and are fundamentally different from the double pyramidal strings of edge and corner shared pyramids encountered in $\mathrm{V_2O_5}$ and in the vanadium bronzes (8). The [BaCl] or [SrCl] chains which wave along

TABLE 2
Positional Parameters and Their Estimated Standard Deviations in $A\mathrm{VO_3CL}$

		x	y	z	U_{eq}
Ba	4c	0.19515(3)	1/4	0.10037(4)	0.01108(7)
V	4c	− 0.04221(8)	3/4	0.4509(1)	0.0076(2)
Cl	4c	0.3951(1)	1/4	0.4276(2)	0.0157(3)
O(1)	8d	0.0958(2)	0.5078(5)	0.4074(4)	0.0103(5)
O(2)	4c	0.3588(4)	3/4	0.2136(5)	0.016(1)
Sr	4c	0.19232(8)	1/4	0.1005(1)	0.0111(2)
V	4c	− 0.0410(2)	3/4	0.4455(2)	0.0078(3)
Cl	4c	0.3933(2)	1/4	0.4323(3)	0.0139(6)
$\mathrm{O_1}$	8d	0.1017(4)	0.5079(7)	0.4064(6)	0.010(1)
$\mathrm{O_2}$	4c	0.3605(7)	3/4	0.2363(8)	0.016(2)
Cd	4c	0.16878(5)	1/4	0.0817(1)	0.0116(2)
V	4c	0.00298(9)	3/4	0.3188(2)	0.0073(3)
Cl	4c	0.2298(2)	1/4	0.4440(3)	0.0165(6)
O(1)	4c	0.0087(4)	1/4	0.3935(8)	0.010(2)
O(2)	4c	0.0916(4)	3/4	0.1800(9)	0.015(2)
O(3)	4c	0.4200(4)	3/4	0.3206(9)	0.020(2)

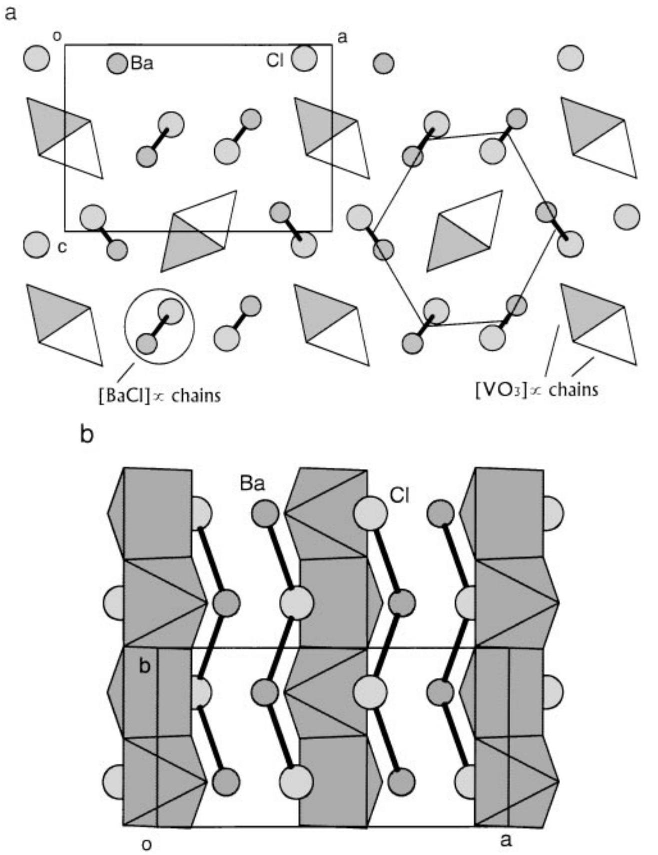

FIG. 1. (a) Projection of the structure of $BaVO_3Cl$ along **b**. In each pyramidal chain running along **b** the pyramids in transconfiguration are shaded and empty triangles, alternately. The hexagon illustrates the distorted honeycomb-type network of $[BaCl]_\infty$ chains containing $[VO_3]_\infty$ chains. (b) Projection of the structure of $BaVO_3Cl$ along **c**.

b (Fig. 1a) show that each chlorine atom has two identical strong bonds with barium (or strontium). Note also that each $[VO_3]_\infty$ chain is surrounded by six $[BaCl]_\infty$ or $[SrCl]_\infty$ chains. The latter form tubes with a distorted hexagonal cross-section (Fig. 1a) containing one $[VO_3]_\infty$ chain each. Thus the structure of these chlorovandates can be described as a distorted honey comb-type network of $[BaCl]_\infty$ or $[SrCl]_\infty$ chains where $[VO_3]_\infty$ chains are interpolated (Fig. 1a).

The $CdVO_3Cl$ structure also exhibits chains of vanadium polyhedra associated with zig-zag chains $[CdCl]_\infty$ running along **b** as shown from the projections of the structure along **b** (Fig. 2a) and along **c** (Fig. 2b). Nevertheless the V polyhedra are of a different nature, forming VO_5 bipyramids. Moreover one observes $[V_2O_6]_\infty$ double chains running

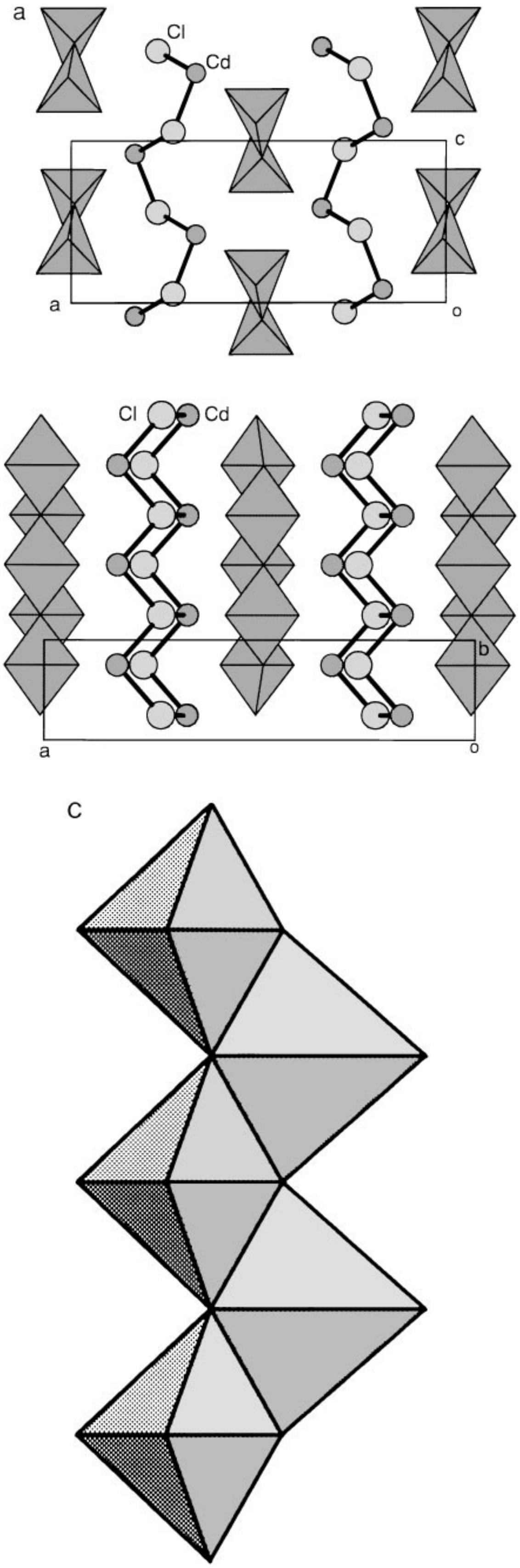

FIG. 2. (a) Projection of the structure of $CdVO_3Cl$ along **b**. (b) Projection of the structure of $CdVO_3Cl$ along **c**. (c) $[V_2O_6]_\infty$ chains in $CdVO_3Cl$ running along **b**.

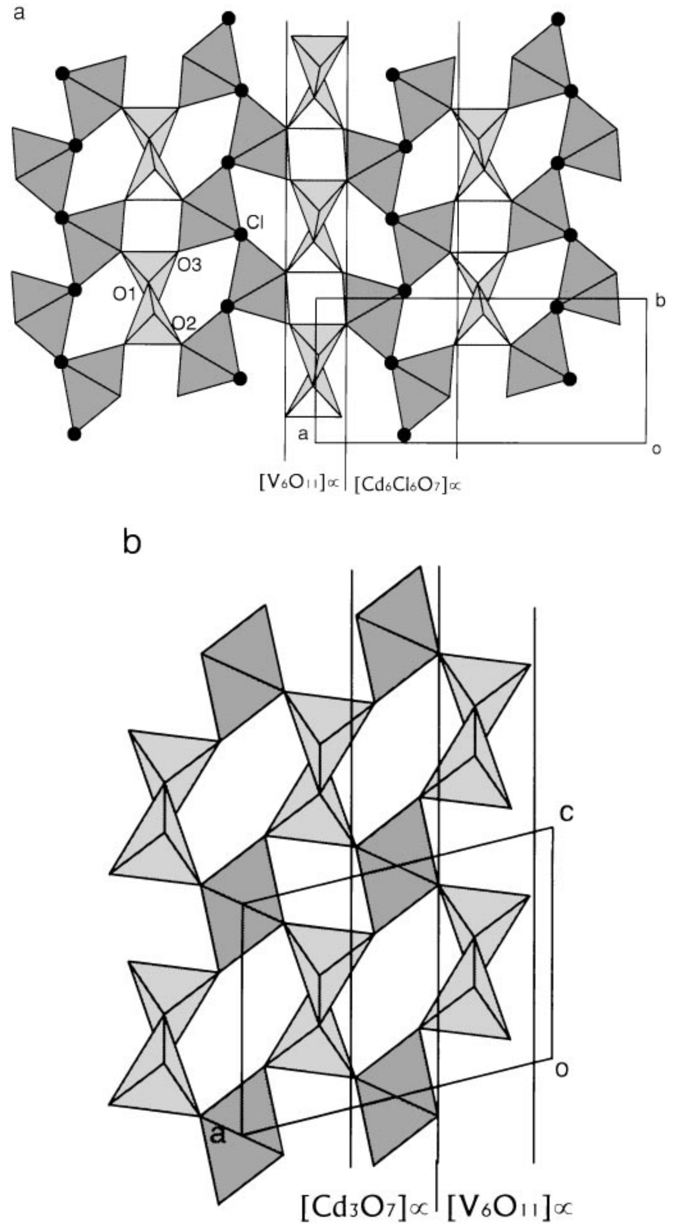

FIG. 3. (a) Projection of the structure of $CdVO_3Cl$ along **b** showing the $[V_6O_{11}]_\infty$ layers of VO_5 pyramids connected with the $[Cd_6Cl_6O_7]_\infty$ rutile-type layers of $CdCl_3O_3$ octahedron. Full circles correspond to the Cl atoms. (b) Projection of the structure of CdV_2O_6 along **b**.

along **b** (Fig. 2), instead of $[VO_3]_\infty$ pyramidal chains for the Ba and Sr chlorovanadates. In the $[V_2O_6]_\infty$ double chains each VO_5 bipyramid shares two edges and two apices with four other bipyramids (2 + 2) (Fig. 2c), so that each VO_5 bipyramid exhibits two free apices. Note that the configuration of these $[V_2O_6]_\infty$ chains is similar to that encountered in $NaVO_3$ (9), KVO_3 H_2O (10), and CdV_2O_6 (11); it is also closely related to the arrangement of the VO_5 pyramids in the V_2O_5 structure (8). In contrast to $BaVO_3Cl$ and $SrVO_3Cl$, the $[CdCl]_\infty$ zig-zag chains in $CdVO_3Cl$ form $[Cd_2Cl_2]_\infty$ layers parallel to (100) (Fig. 2b). In fact such layers can be described as $[Cl_2]_\infty$ layers sandwiched between two $[Cd]_\infty$ layers. As a result cadmium exhibits a distorted octahedral coordination with three Cl neighbors belonging to the $[Cl_2]_\infty$ layer and three O neighbors corresponding to the free apices of the VO_5 bipyramids. As a consequence, the structure of $CdVO_3Cl$ can be described as the association of layers of CdO_3Cl_3 octahedra interconnected with $[V_2O_6]_\infty$ double chains as shown from the projection of the structure along **b** (Fig. 3a). The projection along **a** of one octahedral $[Cd_6Cl_6O_7]_\infty$ layer (Fig. 4) shows that the latter exhibits a distorted rutile type geometry. Thus the structure is built up from $[V_6O_{11}]_\infty$ and rutile $[Cd_6Cl_6O_7]_\infty$ layers stacked along **a** by corner-sharing the VO_5 pyramids and the CdO_3Cl_3 octahedra.

Moreover it is remarkable that this framework forms rather large five-sided tunnels which are unoccupied. In fact the $CdVO_3Cl$ structure is closely related to that of CdV_2O_6 (Fig. 3b) which exhibits similar bipyramidal $[V_6O_{11}]_\infty$ layers, but in which the $[Cd_6Cl_6O_7]_\infty$ layers have been replaced by single $[Cd_3O_7]_\infty$ layers which consist of isolated rutile ribbons of edge sharing CdO_6 octahedra. Consequently, the tunnels that are formed in CdV_2O_6 exhibit a different six-sided section.

THE VO_5 POLYHEDRA

The V–O interatomic distances collected for the three compounds (Table 3) show that the geometry of these polyhedra is close to that generally observed. The VO_5 square pyramids of $BaVO_3Cl$ and $SrVO_3Cl$ exhibit one short apical V–O bond (1.609–1.611 Å) corresponding to the free apex and four longer equatorial bonds of 1.812 to 1.941 Å and of 1.805 to 1.956 Å for Sr and Ba, respectively. In both compounds, the vanadium is off-centered out of the

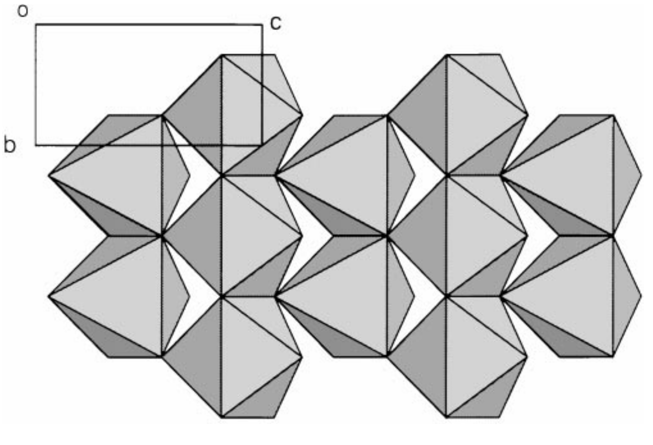

FIG. 4. Projection along **a** of one octahedral rutile $[Cd_6Cl_6O_7]_\infty$ layer.

TABLE 3
Interatomic Distances (Å) and Angles (°) in the Polyhedra for AVO$_3$Cl

V	O(1)	O(1^{i})	O(1^{ii})	O(1^{iii})	O(2)
			SrVO$_3$Cl		
O(1)	1.941(4)	2.429(5)	3.583(7)	2.551(5)	2.919(7)
O(1^{i})	80.6(2)	1.812(4)	2.719(5)	3.583(7)	2.697(6)
O(1^{ii})	145.3(2)	97.2(2)	1.812(6)	2.429(5)	2.697(6)
O(1^{iii})	82.2(2)	145.3(2)	80.6(2)	1.941(4)	2.919(7)
O(2)	110.3(2)	103.9(2)	103.9(2)	110.3(2)	1.609(6)
			BaVO$_3$Cl		
O(1)	1.956(2)	2.424(3)	3.586(5)	2.561(4)	2.936(5)
O(1^{i})	80.2(1)	1.805(3)	2.726(3)	3.586(5)	2.695(4)
O(1^{ii})	144.9(1)	98.1(1)	1.805(3)	2.424(3)	2.695(4)
O(1^{iii})	81.9(1)	144.9(1)	80.2(1)	1.956(3)	2.936(5)
O(2)	110.4(1)	104.1(1)	104.1(1)	110.4(1)	1.611(4)

Symmetry codes for A = Sr and Ba

Sr–Cl = 3.073(2)	i = $-x; 1-y; 1-z$	Ba–Cl = 3.188(1)
Sr–Cl^{iv} = 3.010(1)	ii = $-x; 1/2+y; -z$	Ba–Cl^{iv} = 3.081(1)
Sr–Cl^{v} = 3.010(1)	iii = $x; 3/2-y; z$	Ba–Cl^{v} = 3.081(1)
Sr–Cl^{vi} = 3.022(2)	iv = $1/2-x; -1/2+y; -1/2+z$	Ba–Cl^{vi} = 3.145(1)
Sr–O(1) = 2.688(4)	v = $1/2+x; 1/2+y; -1/2+z$	Ba–O(1) = 2.835(3)
Sr–O(1^{iv}) = 2.786(1)	vi = $-1/2+x; y; 1/2-z$	Ba–O(1^{iv}) = 2.904(3)
Sr–O(1^{vii}) = 2.688(4)	vii = $x; 1/2-y; z$	Ba–O(1^{vii}) = 2.835(3)
Sr–O(1^{viii}) = 2.786(4)	viii = $1/2-x; 1-y; -1/2+z$	Ba–O(1^{viii}) = 2.904(3)
Sr–O(2^{iv}) = 2.592(6)		Ba–O(2^{iv}) = 2.876(3)

CdVO$_3$Cl

V	O(1^{i})	O(1)	O(1^{ii})	O(2)	O(3^{iii})
O(1^{i})	1.976(6)	2.355(6)	2.355(6)	3.311(9)	3.126(8)
O(1)	74.7(2)	1.903(2)	3.662(9)	2.677(6)	2.725(6)
O(1^{ii})	74.7(2)	148.4(3)	1.903(2)	2.677(6)	2.725(6)
O(2)	129.7(3)	96.5(2)	96.5(2)	1.680(6)	2.685(8)
O(3^{iii})	121.0(3)	101.4(2)	101.4(2)	109.4(3)	1.611(6)

Symmetry codes

Cd–Cl = 2.655(2)	i = $-x; 1-y; 1-z$
Cd–Cl^{iv} = 2.600(2)	ii = $x; 1+y; z$
Cd–Cl^{v} = 2.600(2)	iii = $-1/2+x; 3/2-y; 1/2-z$
Cd–O(2^{vi}) = 2.294(4)	iv = $1/2-x; -1/2+y; -1/2+z$
Cd–O(2) = 2.294(4)	v = $1/2-x; 1/2+y; -1/2+z$
Cd–O(3^{iv}) = 2.262(6)	vi = $x; -1+y; z$

equatorial plane of the VO$_5$ square pyramid by 0.542 Å for SrVO$_3$Cl and by 0.547 Å for BaVO$_3$Cl.

In the VO$_5$ bipyramids of CdVO$_3$Cl, one observes two short V–O bonds corresponding to the two free apices, i.e., to the oxygen atoms shared with the CdO$_3$Cl$_3$ octahedra (1.611 and 1.681 Å) and three longer ones corresponding to the oxygen atoms shared between the pyramids (1.903 to 1.976 Å). Note that the vanadium sits in the equatorial plane of the bipyramid and that the V–V distance between two edge-shared bipyramids is rather long, i.e., equal to 3.083(2) Å.

THE DIVALENT CATION POLYHEDRA

Barium and strontium are linked to four chlorine atoms located at distances ranging from 3.081 to 3.188 Å and from 3.010 to 3.073 Å, respectively (Table 3), in agreement with the ionic radii of Ba^{2+}, Sr^{2+}, and Cl^{-}. The chlorine environment can be described as distorted BaCl$_4$ or SrCl$_4$ tetrahedra, and reciprocally, one observes distorted ClBa$_4$ and ClSr$_4$ tetrahedra. Besides chlorine, each barium and strontium atom has five oxygen neighbors at distances ranging from 2.835 to 2.904 Å and from 2.592 to 2.786 Å, respectively. The oxygen environment of these cations can then be described as distorted BaO$_5$ and SrO$_5$ square pyramids. Thus, the global coordination of barium and strontium can be described by ACl$_4$O$_5$ polyhedra sharing their edges in such a way that they form a 3D network where V atoms are inserted.

The CdCl$_3$O$_3$ octahedra are strongly distorted with three Cd–Cl bonds ranging from 2.600 to 2.655 Å and three Cd–O bonds ranging from 2.262 to 2.294 Å.

CONCLUDING REMARKS

This study shows the possibility of associating ACl chains with VO$_3$ or V$_2$O$_6$ chains of edge-sharing VO$_5$ pyramids for the generation of original chain or layered structures. Among those oxides the oxychloride CdVO$_3$Cl is susceptible to exhibit intercalation owing to the existence of empty five-sided tunnels. Attempts to introduce lithium in those tunnels, by synthetizing the compounds Li$_x$CdVO$_3$Cl, using direct methods have been unsuccessful to date. Reaction with butyl lithium leads to a change of color, the CdVO$_3$Cl phase color becoming brown. Nevertheless the amount of lithium in the phase, determined from atomic absorption, remains small ($x < 0.10$). The electrochemical intercalation of lithium in this phase will be investigated.

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