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Coordination Intercalation of $NbAsO_5$ with Alkali-Metal Chloride. Synthesis, Structure, and Spectroscopy of Two New Layered Niobium(V) Arsenate Compounds, $ANbAsO_5Cl$ (A = Rb, Cs)

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Via a direct reaction of $NbAsO_5$ and ACl (A = Rb, Cs), a new family of layered niobium(V) arsenate compounds, $ANbAsO_5Cl$, was synthesized. Single crystals of these new phases were grown by employing either a single flux of the respective chloride or a eutectic flux of ACl/A′Cl (A′ = Na, K). The cell constants are $a = 6.6605(6)$ Å, $c = 7.680(2)$ Å for $RbNbAsO_5Cl$ ($Z = 2$, tetragonal, $P4/n$); $a = 6.662(2)$ Å, $b = 7.879(3)$ Å, $c = 6.663(1)$ Å, $\beta = 90.01(2)°$ for $CsNbAsO_5Cl$ ($Z = 2$, monoclinic, $P2/n$). The single-crystal X-ray structures show that the title compounds adopt a layered framework that consists of alternately stacked $NbAsO_5$ slabs and (100) ACl rock salt sheets. The Nb^{5+} cation resides in a distorted [5+1] NbO_5Cl octahedral coordination environment. The formation of a layered structure can be envisioned if the $NbAsO_5$ framework is chemically dissected by molten alkali-metal chloride along the planes of long (weak) Nb−O bonds. Topologically, the Cl^- anions insert into a three-dimensional framework to replace the long Nb−O bonds (2.23 Å) by coordination intercalation. The $[NbAsO_5Cl]$ slab adopts the polyhedral arrangement of the single $[NbAsO_5]$ slab found in the monoclinic α-$NbAsO_5$ phase. The chloride capped niobium arsenate anionic slab $[NbAsO_5Cl]^-$ is neutralized by the countercation A^+. This paper reports the synthesis, structure, and UV−vis diffuse reflectance spectroscopy of the title compounds.

Introduction

Chemical intercalation has been fundamentally demonstrated by insertion of guest species into host lattices containing either a van der Waals gap or an empty tunnel.[1] These structural characteristics provide a certain degree of framework openness which permits foreign atoms or ions to readily diffuse into or out of the crystal lattice. It is a convenient chemical modification method yielding new materials with enhanced physical properties. The graphite and TiS_2 intercalation compounds, for instance, are classical examples exhibiting improved electrical conductivity via redox intercalation.[2,3] Several recent examples also have shown that chemical intercalation can be applied to the more compacted frameworks such as close-packed spinel oxide $Li_xMn_2O_4$ and layered perovskite oxide $A^ILaNb_2O_7$ (A = Li, Na, K, Rb, Cs, NH_4).[4]

Coordination intercalation facilitates a new dimension for materials synthesis. This type of reaction has been demonstrated by the formation of inorganic/organic hybrid materials. These hybrid materials have recently received growing attention because of their sorptive and catalytic properties.[5] The extended structure can be characterized by a quasi-two-dimensional array of alternating organic and inorganic layers. One of the common structural classes exhibits a direct coordination between organic ligands and transition metal centers of the inorganic layers, e.g., $VOXO_4(C_5H_5N)$ (X = P, As).[6] The vanadium(V) compounds can be prepared through coordination intercalation of $VOXO_4$ with pyridine; no single crystals have yet been isolated. The structural information has thus far been estimated through infrared and powder X-ray diffraction analyses. The proposed structural model has a $VOXO_4$ layer essentially identical with that of the mother compound. The layers are, however, separated by breaking the long axial V−O bond (2.85 Å) of the VO_6 octahedron via replacing the oxygen from the adjacent layer in the coordination sphere with a pyridine molecule.

We have had an extended interest in the synthesis of low-dimensional transition metal silicates, phosphates, and arsenates.[7] The newly isolated quasi-two-dimensional niobium(V) arsenates, $ANbAsO_5Cl$ (A = Rb, Cs), can be considered a derivative of α-$NbAsO_5$, formed by coordination intercalation with ACl salt. Niobium arsenate, $NbAsO_5$, has two polymorphs that have been structurally characterized recently by single-crystal X-ray diffraction studies.[8] In the α-form, NbO_6 chains are straight

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[1] Whittingham, M. S.; Jacobson, A. J. *Intercalation Chemistry*; Academic Press: New York, 1982.

[2] The compounds of graphite intercalated by the alkali metals are described in the following article as well as the references cited in ref 1: Novikov, Y. N.; Volpin, M. E. *Russ. Chem. Rev.* **1971**, *40*, 733.

[3] For TiS_2 intercalation, see the following reviews: (a) Rouxel, J. In *Physics and Chemistry of Compounds with Layered Structures*; Levy, F., Ed.; Reidel Publishers: Dordrecht, The Netherlands, 1979; p 201. (b) Whittingham, M. S. *Prog. Solid State Chem.* **1978**, *12*, 41.

[4] (a) Spinel-type $Li_xMn_2O_4$: Goodenough, J. B.; Thackeray, M. M.; David, W. I. F.; Bruce, P. G. *Rev. Chim. Miner.* **1984**, *21*, 435. (b) Layered perovskite $A^ILaNb_2O_7$: Gopalakrishnan, J.; Bhat, V.; Raveau, B. *Mater. Res. Bull.* **1987**, *22*, 413.

[5] Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Lewandowski, J. T. *Inorg. Chem.* **1984**, *23*, 3842 and references therein.

[6] Johnson, J. W.; Jacobson, A. J.; Brody, J. F.; Rich, S. M. *Inorg. Chem.* **1982**, *21*, 3820.

[7] Hwu, S.-J.; Willis, E. D. *J. Solid State Chem.* **1991**, *93*, 69. (b) Serra, D. L.; Hwu, S.-J. *J. Solid State Chem.* **1992**, *98*, 174. (c) Wang, S.; Hwu, S.-J. *J. Am. Chem. Soc.* **1992**, *114*, 6920. (d) Serra, D. L.; Hwu, S.-J. *J. Solid State Chem.* **1992**, *101*, 32. (e) Wang, S.; Hwu, S.-J. *Inorg. Chem.* **1995**, *34*, 166. (f) Etheredge, K. M. S.; Hwu, S.-J. *Inorg. Chem.* **1995**, *34*, 1495. (g) Wang, S.; Hwu, S.-J.; Paradis, J. A.; Whangbo, M.-H. *J. Am. Chem. Soc.* **1995**, *117*, 5515. (h) Etheredge, K. M. S.; Hwu, S.-J. *Inorg. Chem.* **1996**, *35*, 1474. (i) Etheredge, K. M. S.; Hwu, S.-J. *Inorg. Chem.* **1996**, *35*, 5278.

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($\angle$Nb−O−Nb = 180.0(1)°) and each AsO_4 tetrahedron links four different octahedral chains. In the β form, the AsO_4 links three chains to give rise to a smaller angle ($\angle$Nb−O−Nb = 151.1(2)°). As a result, the former possesses a more compact framework than the latter, as shown by calculated densities, 4.73 vs 4.32 g/cm^3, respectively. The title compounds adopt the polyhedral arrangements of the single slab in α-$NbAsO_5$ and exhibit a closely related coordination framework to the proposed structure of $VOXO_4(C_5H_5N)$.

The title compounds isolated in the $Nb_2O_5 \cdot As_2O_5 \cdot ACl$ systems, where A = Rb, Cs, are new. This paper reports the synthesis, single-crystal structure, and UV−vis diffuse reflectance spectroscopy of $ANbAsO_5Cl$. The topotactic chemical dissection reaction of $NbAsO_5$ with ACl is described. In addition, the structural relationship to α-$NbAsO_5$ is discussed.

Experimental Section

Synthesis. During the study of the reduced Cs−Nb(IV)−As−O system, platelike colorless crystals of $CsNbAsO_5Cl$ were first isolated. The cesium compound and its rubidium analogue were then deliberately synthesized by direct reaction of β-$NbAsO_5$ with either the respective ACl or ACl/A′Cl (A = Rb, Cs; A′ = Na, K, respectively) eutectic flux. Although no reaction using α-$NbAsO_5$ was carried out because the precursor could not be synthesized by conventional methods, it is intuitively anticipated that a topotactic reaction is possible.

For the synthesis of the $CsNbAsO_5Cl$ single crystal, a typical reaction was carried out as follows: 0.0706 g (0.5652 mmol) of NbO_2 (Aesar, 99+%) and 0.1299 g (0.5652 mmol) of As_2O_5 (Aesar, 99.9%) were ground together and directly mixed with predried 0.1598 g (2.144 mmol) of KCl (Aldrich, 99.99+%) and 0.8423 g (5.003 mmol) of CsCl (Aesar, 99.00%). The reaction mixture was placed in a carbon-coated silica ampule which was then sealed under vacuum. The reaction was slowly heated at a rate of 5 °C per hour to 800 °C with an isotherm at intermediate temperatures of 300 °C and every 100 °C increment. After a week at 800 °C, the reaction was cooled at a rate of 3 °C per hour to 500 °C followed by furnace cooling. The reaction products include colorless, platelike $CsNbAsO_5Cl$ crystals.

After the structure determination, alternative methods to synthesize the title compounds in stoichiometric yield and single crystals were performed. These two new phases were prepared by using a stoichiometric amount of Nb_2O_5, As_2O_5, and the respective salt, ACl, at 800 °C. The direct reaction using an oxidized precursor, β-$NbAsO_5$, and ACl resulted in single crystals of the title compounds and a trace amount of unidentifiable powder (see powder pattern reported in Supporting Information).

Follow-up reactions using the β-$NbAsO_5$ precursor and an eutectic flux, such as RbCl/NaCl and CsCl/KCl, produced better quality crystals in size and morphology. A new phase "$NaNbAsO_5Cl$", with an estimated formula based on EDAX (energy dispersive analysis by X-ray), was isolated from the $BaCl_2$/NaCl eutectic flux, and its structure is still under investigation.

Structure Determination. Powder X-ray Diffraction. The data were collected at room temperature from a ground powder of selected crystals. These patterns adopt a great resemblance to that of $NbAsO_5 \cdot 4H_2O$ reported previously.[9] The indexed cell constants for the tetragonal $RbNbAsO_5Cl$ (a = 6.664(1) Å, c = 7.679(3) Å, V = 341.0(2) Å^3) are comparable with those for the tetragonal $NbAsO_5 \cdot 4H_2O$ (a = 6.65 Å, c = 7.93 Å, V = 350.68 Å^3) reported by Chernorukov et al.[9] This close comparison suggests that these two structures could be related. It was postulated by Chernorukov et al.[9] that the $NbAsO_5 \cdot 4H_2O$ phase possesses a stacking $NbOAsO_4$ slab structure with water molecules incorporated between the layers.

Table 1. Crystallographic Data[a] for $ANbAsO_5Cl$ (A = Rb, Cs)

empirical formula	$RbNbAsO_5Cl$	$CsNbAsO_5Cl$
fw (amu)	368.75	416.18
space group	$P4/n$ (No. 85)	$P2/n$ (No. 13)
a, Å	6.6605 (6)	6.662 (2)
b, Å	−	7.879 (3)
c, Å	7.680 (2)	6.663 (1)
β, deg	−	90.01 (2)
V, Å^3	340.72 (9)	349.6 (2)
Z	2	2
T, K	298	298
λ, Å	0.710 73	0.710 73
ρ_{calcd}, g cm^{-3}	3.594	3.953
linear abs coeff, cm^{-1}	140.24	118.81
$R(F_o)$[b]	0.035	0.035
$R_w(F_o)$[c]	0.036	0.040

[a] The cell constants are refined in each designated crystal system (Rb, 25 reflections, 29.6 < 2θ < 45.3°; Cs, 25 reflections, 22.5 < 2θ < 37.4°). [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F) + aF^2]$ (where a = 0.01 for Rb and 0.007 for Cs analogue).

Single-Crystal X-ray Diffraction. The two single crystal structures were characterized in a similar manner. Due to the limited space, we report only the structure data for the rubidium compound. The experimental details for the cesium analogue can be acquired from the Supporting Information.

Good-quality crystals of $RbNbAsO_5Cl$ were physically examined and selected under an optical microscope equipped with a polarizing light attachment. The data crystal was mounted on a glass fiber with epoxy for the single-crystal X-ray study. The diffraction data were collected at room temperature on a Rigaku AFC7R four-circle diffractometer (Mo Kα, λ = 0.710 73 Å) equipped with a graphite monochromator. Crystallographic data of the title compound are given in Table 1. The initial unit cell parameters and the orientation matrix were determined by a least-squares fit of 18 reflections selected from random search with 12.2 < 2θ < 20.4°. Data were collected using an ω−2θ scan mode at 8°/min (≤7 rescans). A total of 2680 reflections ($2\theta_{max}$ = 65°) were collected on the primitive cell from four octants (h, ±k, ±l), of which reflections with $F > 6\sigma(F)$ were used for the structural solution. No detectable decay was observed during the data collection, according to the intensities of three standard reflections (−2, 2, 2; −2, 2, 0; −2, 0, 2) which were measured every 100 reflections. Lorentz−polarization and empirical absorption corrections[10] (ψ scans) were applied to the data. On the basis of the Laue class 4/m and extinction conditions, the structure was solved in the space group $P4/n$ (No. 85). The structure was solved by direct methods with SHELX-86[11] and refined on $|F|$ with SHELXTL-Plus[12] by least squares, full-matrix techniques.[13] Scattering factors for all atoms were taken from the source program. The axial photos showed no evidence of superstructure. The positional and thermal parameters for the $RbNbAsO_5Cl$ phase are reported in Table 2. The selected bond distances and angles are listed in Table 3.

Qualitative analysis of the data crystal was carried out by EDAX and only showed the presence of the respective elements for the title compounds.

Infrared Spectroscopy. The IR spectra were taken in the range of 1200−400 cm^{-1} from the ground powder of selected crystals which were pressed into a disk with KBr. The data were recorded on the Perkin-Elmer 1600 Series FTIR spectrometer with 16 scans and 2.0 cm^{-1} increments.

UV−Vis Diffuse Reflectance Spectroscopy. Optical absorption spectra were obtained from a PC-controlled Shimadzu UV-3100 UV−vis−near-IR spectrometer equipped with an integrating sphere. $BaSO_4$

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(8) Ulutagay, M. M.S. Thesis, Clemson University, Clemson, SC, 1997.

(9) Chernorukov, N.; Egorov, N. P.; Korshunova, I. A. *Inorg. Mater. (Engl. Trans.)* **1979**, *15*, 266.

(10) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

(11) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: London, 1985; pp 175−189.

(12) Sheldrick, G. M. *SHELXTL-PLUS, Version 4.2.1. Structure Determination Software Programs*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1990.

(13) Busing, W. R.; Martin, K. O.; Levy, H. A. *ORFLS*; Report ORNL-TM-305; Oak Ridge National Laboratory: Oak Ridge, TN, 1962.

Table 2. Positional and Thermal Parameters for $RbNbAsO_5Cl$

atom	Wyckoff position	x	y	z	U_{eq} (Å^2)^a
Rb	2b	$^1/_4$	$^3/_4$	$^1/_2$	0.030(1)
Nb	2c	$-^1/_4$	$^3/_4$	0.1003(1)	0.012(1)
As	2a	$^1/_4$	$^3/_4$	0	0.012(1)
Cl	2c	$-^1/_4$	$^3/_4$	0.4462(3)	0.023(1)
O(1)	2c	$-^1/_4$	$^3/_4$	−0.1214(9)	0.030(1)
O(2)	8g	0.0522(3)	0.7500(3)	0.1345(4)	0.019(1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $RbNbAsO_5Cl^a$

	NbO_5Cl		
$Nb-O(1)^a$	1.703(7)	$Nb-Cl^a$	2.656(3)
$Nb-O(2)^{a,b,c,d}$	2.030(2) × 4		
$O(1)^a-Nb-O(2)^{a,b,c,d}$	97.4(1) × 4	$Cl^a-Nb-O(1)^a$	180.0(1)
$O(2)^a-Nb-O(2)^b$	165.1(2)	$Cl^a-Nb-O(2)^{a,b,c,d}$	82.6(1) × 4
$O(2)^c-Nb-O(2)^d$	165.1(2)	$O(2)^{a\text{ or }b}-Nb-O(2)^{c,d}$	89.0(1) × 4
	AsO_4		
$As-O(2)^{a,e,f,g}$	1.674(2) × 4		
$O(2)^a-As-O(2)^e$	103.8(2)	$O(2)^{a\text{ or }e}-As-O(2)^{f,g}$	112.4(1) × 4
$O(2)^f-As-O(2)^g$	103.8(2)		
	RbO_4Cl_4		
$Rb-O(2)^{a,e,h,i}$	3.101(3) × 4	$Rb-Cl^{a,j,k,l}$	3.356(1) × 4
$O(2)^a-Rb-O(2)^e$	50.3(1)	$Cl^a-Rb-O(2)^{h,i}$	96.4(1) × 2
$O(2)^h-Rb-O(2)^i$	50.3(1)	$Cl^j-Rb-O(2)^{h,i}$	96.4(1) × 2
$O(2)^{a\text{ or }e}-Rb-O(2)^{h,i}$	145.0(1) × 4	$Cl^k-Rb-O(2)^{a,e}$	96.4(1) × 2
$Cl^a-Rb-Cl^j$	165.9(1)	$Cl^l-Rb-O(2)^{a,e}$	96.4(1) × 2
$Cl^k-Rb-Cl^l$	165.9(1)	$Cl^a-Rb-O(2)^e$	108.1(1)
$Cl^{a\text{ or }j}-Rb-Cl^{k,l}$	90.9(1) × 4	$Cl^j-Rb-O(2)^a$	108.1(1)
$Cl^a-Rb-O(2)^a$	57.8(1)	$Cl^k-Rb-O(2)^h$	108.1(1)
$Cl^j-Rb-O(2)^e$	57.8(1)	$Cl^l-Rb-O(2)^i$	108.1(1)
$Cl^k-Rb-O(2)^i$	57.8(1)	$Cl^l-Rb-O(2)^h$	57.8(1)

[a] Symmetry codes: a, $+x$, $+y$, $+z$; b, $-1/2 - x$, $3/2 - y$, $+z$; c, $1/2 - y$, $1+x$, $+z$; d, $y - 1$, $1/2 - x$, $+z$; e, $1/2 - x$, $3/2 - y$, $+z$; f, $-1/2+y$, $1 - x$, $-z$; g, $1 - y$, $1/2+x$, $-z$; h, $-1/2+y$,$1 - x$, $1 - z$; i, $1 - y$, $1/2+x$, $1 - z$; j, $x+1$, $+y$, $+z$; k, $-x$, $1 - y$, $1 - z$; l, $-x$, $2 - y$, $1 - z$.

was used as a reflectance standard. UV−vis diffuse reflectance spectra of the title compounds were taken in the range of 200 nm (6.2 eV) to 2500 nm (0.50 eV). Data were collected in reflectance (R%) mode and manually converted to arbitrary absorption units (α/s) by the relationship $A = \alpha/s = (1 - R\%/100)^2/2(R\%)$.[14]

Results and Discussion

The title compounds draw a close structural resemblance with the tetragonal $NbAsO_5{\cdot}4H_2O$, whose proposed structure consists of slabs of square-pyramidal NbO_5 and tetrahedral AsO_4.[9] One of the water molecules coordinates with Nb, and the remaining reside in the voids between the $[NbAsO_5]$ slabs. In the structure of title compounds, $ANbAsO_5Cl$, the chloride anion, Cl^-, replaces the water molecule along with the countercation, A^+. As shown by the representative $RbNbAsO_5Cl$ structure (Figure 1), the RbCl layer resides in the interlayer with the Cl^- anions directly bound to Nb.

The formation of a layered structure can be considered the result of ACl salt insertion and subsequently the structural formula can be written as $NbAsO_5{\cdot}ACl$. The schematic drawing shown in Figure 2 illustrates the coordination intercalation of the three-dimensional framework of α-$NbAsO_5$ with RbCl. The mother framework consists of corner-shared NbO_6 octahedral chains interlinked by AsO_4 tetrahedra. The resulting structure forms discrete NbO_5Cl octahedra where chlorine atoms substitute for oxygen to give rise to the observed layer separation. The corresponding vertical axis expands from 4.08 Å in α-$NbAsO_5$[8] to 7.68 Å in $RbNbAsO_5Cl$.

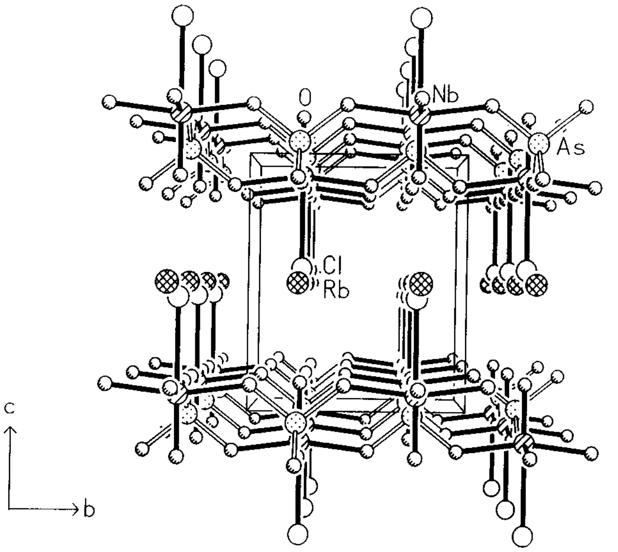

Figure 1. Perspective view of $RbNbAsO_5Cl$ along the a axis. The unit cell is outlined. The Nb−O and Nb−Cl bonds are drawn as thick lines, and As−O bonds are drawn as double lines.

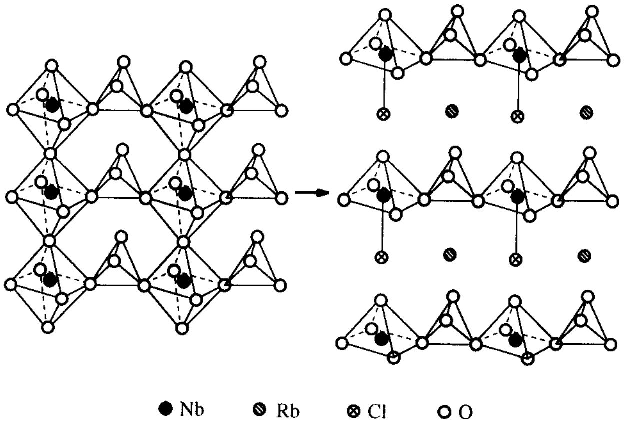

Figure 2. Schematic representation of the coordination intercalation of $NbAsO_5$ with the RbCl salt. The NbO_6 octahedral chain in the $NbAsO_5$ lattice (left) is broken down by replacing the long Nb−O bonds with Nb−Cl bonds to form the layered $RbNbAsO_5Cl$ structure (right).

The slab framework of the title compound forms a tetragonal net that adopts the same connectivity as the single-slab configuration of the monoclinic α-$NbAsO_5$ phase. As shown in Figure 3, the two slab structures are made of alternating Nb-centered octahedra and AsO_4 tetrahedra. The A-site cations, omitted for clarity in Figure 3a, reside directly above or below the As^{5+} cations to form the ACl sheet that adopts the (100) plane of the rock salt lattice. The $[NbAsO_5Cl]$ slab (Figure 3a) is stretched out to form a tetragonal net, presumably to match the (100) ACl lattice. Also, as mentioned above, the title compounds were synthesized via utilizing β-$NbAsO_5$ as a precursor, which is different than the α-phase in terms of the structural connectivity between the NbO_6 octahedral chains and AsO_4 tetrahedra (Figure 4). It is therefore reasonable to propose that a structural rearrangement occurs during the construction of the tetragonal net. The arrangement involves a rotation of AsO_4 groups and connected NbO_5Cl octahedra.

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(14) (a) Kubelka, P.; Munk, F. Z. *Tech. Phys.* **1931**, *12*, 593. (b) Kubelka, P. *J. Opt. Soc. Am.* **1948**, *38*, 448.

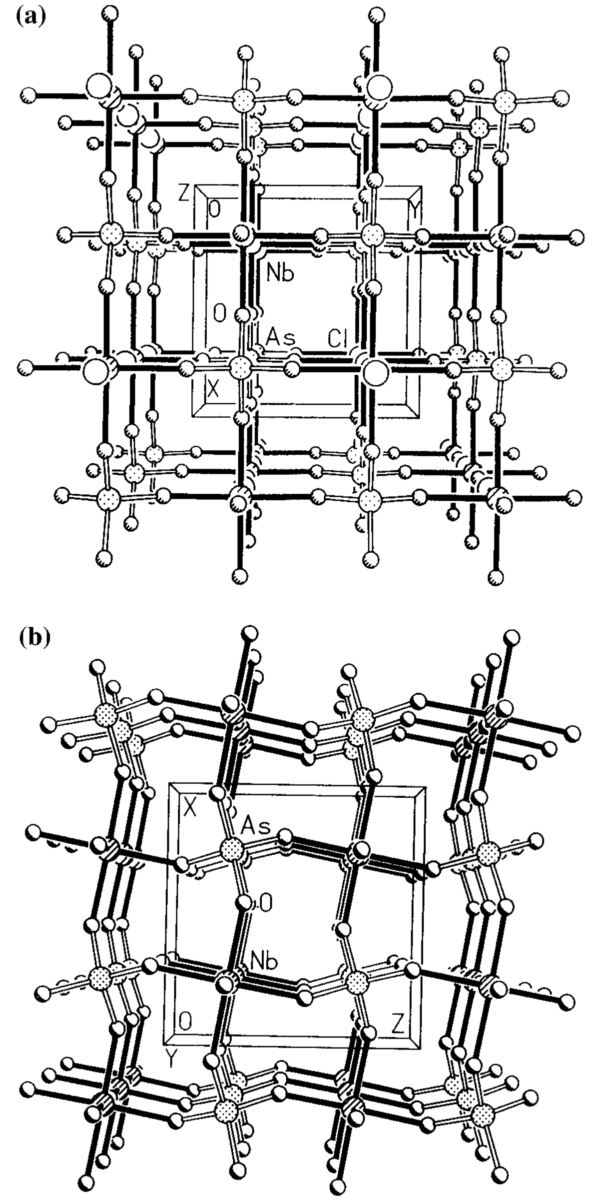

Figure 3. (a) Projected view of the slab structure [NbAsO$_5$Cl] showing the tetragonal net. (b) For comparison, a projected view of α-NbAsO$_5$ extended along the stacking direction (*b* axis) is given.

The Nb center has a distorted [5+1] octahedral geometry in which a short Nb−O(1) bond is in an apical position opposite to the long Nb−Cl bond. The Nb−O(1) bond, 1.703(7) Å (Table 3), is much shorter than 1.99 Å, the sum of Shannon crystal radii of six-coordinate Nb^{5+} (0.78 Å) and O^{2-} (1.21 Å).[15] This short bond distance is commonly seen in the Nb(V) oxides and is similarly observed in the α- and β-NbAsO$_5$ structures, 1.738(7) and 1.760(3) Å, respectively.[8] The four equatorial Nb−O(2) bonds, otherwise, have a regular distance of 2.030(2) Å. The strong interaction between Nb and O(1) results in a relatively weak and subsequently long Nb−Cl bond. The Nb−Cl bond distance, 2.656(3) Å, is longer than the expected value, 2.45 Å, the sum of Shannon crystal radii of six coordinate Nb^{5+} (0.78 Å) and Cl$^-$ (1.67 Å).[15] This is also longer than the reported Nb−Cl bond, e.g., 2.250−2.555(6) Å in NbCl$_5$.[16] The observed bond distances for the AsO$_4$ tetrahedra are 1.674(2) Å, similar to those in previously investigated arsenic phases.[17] The rubidium cation resides between the layers and coordinates to four oxygen and four chlorine atoms (Figure 5). One slab above and one slab below the puckered (100) rock salt sheet each contributes two of the oxygen atoms that bond to Rb$^+$. The Rb−O(2) bond distance is 3.101(3) Å, which is slightly longer than the sum of Shannon radii (2.96 Å) of eight-coordinate Rb$^+$ (1.75 Å) and O^{2-} (1.21 Å).[15] A synergistic effect gives rise to the Rb−Cl distance, 3.356(1) Å, which is slightly shorter than the sum of Shannon radii (3.42 Å)[15] of eight-coordinate Rb$^+$ (1.75 Å) and Cl$^-$ (1.67 Å).

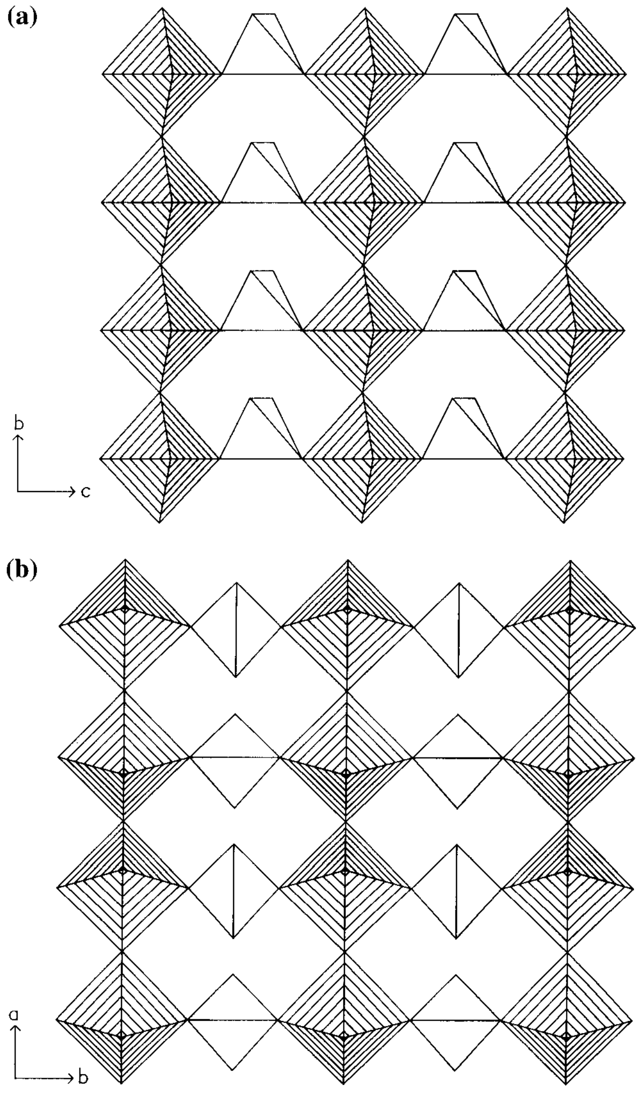

Figure 4. Polyhedral representations of partial structures of (a) α-NbAsO$_5$ and (b) β-NbAsO$_5$.

Both Rb and Cs compounds adopt the same structure with an exception that the Cs analogue possesses a disordering in the axial Nb−(O,Cl) ligands. Consequently, the CsNbAsO$_5$Cl structure was resolved in a monoclinic lattice with a nearly orthogonal β angle, 90.01° (Table 1). The Cs structure has the niobium atom off center and distributed over two sites, Nb(1) and Nb(2), along the pseudo 4-fold axis of the [5+1] octahedron. This results in a short Nb(1)−Nb(2) separation distance, 0.30(3) Å. To avoid an unreasonably short Nb−O(1) bond, the final positions of corresponding apical oxygen and chlorine atoms are modeled concurrently with the disordered Nb.[18] This results

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(15) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.

(16) Zalkin, A.; Sands, E. *Acta Crystallogr.* **1958**, *11*, 615.

(17) Mackay, R.; Wardojo, T. A.; Hwu, S.-J. *J. Solid State Chem.* **1996**, *125*, 255.

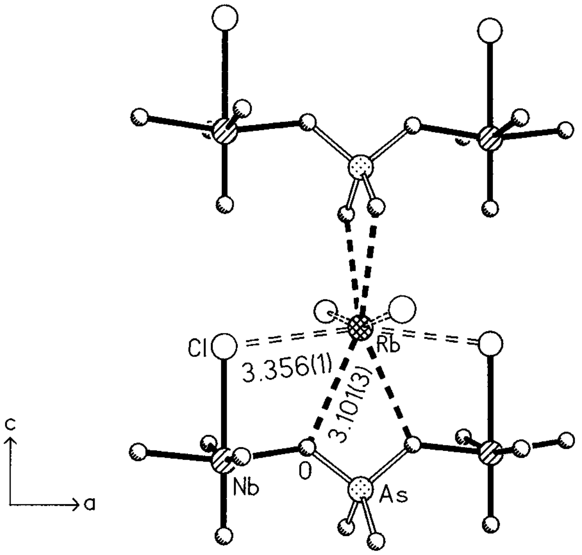

Figure 5. Partial structure of $RbNbAsO_5Cl$ showing the coordination of the Rb^+ cation in RbO_4Cl_4 attributed to the two neighboring [$NbAsO_5Cl$] slabs.

in a set of two [5+1] octahedra with the atoms being numbered such that Nb(1) is coordinated to O(1) and Cl(1) while Nb(2) is coordinated to O(2), Cl(2) in the apical positions (Figure 6). The refined occupancy is of the ratio 44:56 for all three atoms (Nb, O, Cl). The observed bond distances for the AsO_4 tetrahedron are 1.678 and 1.682(5) Å, similar to those reported in the Rb structure.

The structural disorder may be due to the large size of the Cs^+ cation. In the Rb structure, the Nb−O−As linkage is already stretched out to accommodate the dimension of the (100) sheet of the RbCl lattice. To incorporate a larger Cs^+ cation, instead of stretching the lattice network beyond its limitation, the [$NbAsO_5Cl$] slab structure is distorted (puckered) along the apical direction of the Nb-centered octahedra. In the CsO_4Cl_4 coordination, the equatorial oxygens, O(3) and O(4), give four reasonable Cs−O bond distances with two sets at 3.194 and 3.190(6) Å, respectively. These distances are slightly longer than 3.09 Å, the sum of Shannon crystal radii of eight-coordinate Cs^+ (1.88 Å) and O^{2-} (1.21 Å).[15] The disorder causes, however, a significant distortion in the CsO_4Cl_4 coordination where the two long Cs−Cl(1) bond distances are 4.132(7) Å, much longer than the sum of Shannon crystal radii (3.55 Å) of eight coordinate Cs^+ (1.88 Å) and Cl^- (1.67 Å),[15] and the two short Cs−Cl(2) bond distances are 3.370(2) Å.

The bond valence sum calculations were performed to examine the formal valence of the cations in both compounds.

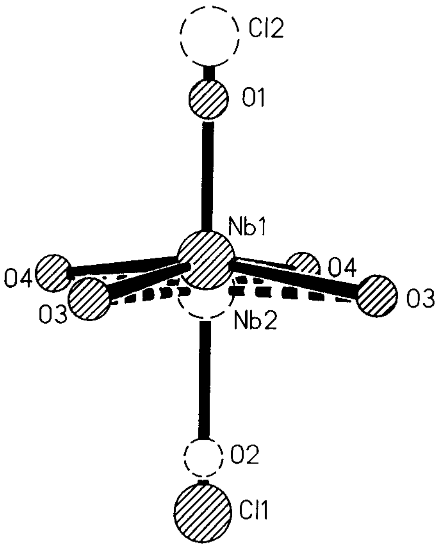

Figure 6. Disordered NbO_5Cl octahedron in the $CsNbAsO_5Cl$ structure. Shaded circles represent a subset of NbO_5Cl with 44% occupancy. The open circles along with the waist oxygen atoms form the second subset of NbO_5Cl with 56% occupancy.

Using the empirical relationship developed by Brown and Altermatt, the valence of a given atom is calculated from the sum of the individual bond strengths of metal−oxygen and metal−chlorine bonds.[19] Niobium−chlorine bond strengths are not given in the related literature. Using the equations derived by the same authors in the same reference, the Nb−Cl bond strength was calculated. The calculated bond valence sums are in agreement with the formal oxidation states of A^+, Nb^{5+}, and As^{5+}. The bond valence sum for Nb^{5+} in the Cs analogue was calculated by using a mixed 44% and 56% octahedral coordination environment.

The infrared results were consistent with what would be expected. In the $RbNbAsO_5Cl$ spectra, a narrow band at ~1000 cm^{-1} corresponded to the stretching vibrations of the isolated Nb−O bonds.[8,20] For $CsNbAsO_5Cl$, the corresponding band was split into two at 1010 and 980 cm^{-1}. This is likely the result of the disordered Nb atom. The As−O vibrational frequencies associated with the $[AsO_4]^{3-}$ group are observed in broad bands centered at ~820 (s) and ~565 (w) cm^{-1}.[20] The shoulder observed in the cesium analogue at ~890 cm^{-1} is again due to the structural disordering discussed above.

The UV−vis spectra (Figure 7) are consistent with the observed structure. The absorptions centered at ~5.6 eV (~222 nm), for $RbNbAsO_5Cl$, and 4.45 eV (~279 nm), for $CsNbAsO_5Cl$, correspond to LMCT bands originating from the AsO_4 group. These are in the range of values of the earlier studied alkaline-earth arsenates,[8,21−22] e.g., at ~4.35 eV (~285 nm) for $NaNb_2AsO_8$,[22] 4.2 eV (~295 nm) for α-$NbAsO_5$, and ~5.4 eV (~230 nm) for β-$NbAsO_5$.[8] The peak corresponding to the oxo oxygen LMCT band (observed at ~3.6 eV in β-$NbAsO_5$, Figure 7c) is missing in Figure 7a and presumably in Figure 7b as well. This is because neither Nb−O−Nb nor Nb−Cl−Nb is present. All equatorial oxygens around Nb are connected to arsenic in the

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(18) Each NbO_5Cl octahedron can be described by a unique set of bond distances and angles. Nb(1)/Nb(2) has octahedral geometry and is coordinated to O(1)/O(2) in the apical position with approximately equivalent bond distances of 1.70(4) or 1.70(3) Å, respectively. The nonbonding distances between Nb(1)−O(2) and Nb(2)−O(1) are 2.00(4) and 2.00(3) Å, respectively. The short Nb−O bond distance is shorter than those in the rubidium analogue, but more reasonable than 1.41(5) Å, the Nb−O distance obtained when the structure was refined in *P*4/*n*. The equatorial Nb(1)−O(3,4) and Nb(2)−O(3,4) bond distances are 2.008(4), 2.009(4) and 2.021(4), 2.022(4) Å, respectively. The Nb(1)−Cl(1) and Nb(2)−Cl(2) bond distances are 2.59(2) Å, and 2.63(2) Å, respectively, which are comparable with those of the rubidium analogue (2.656(3) Å). The nonbonding cross distances between Nb(1)−Cl(2) and Nb(2)−Cl(1), however, are 2.33(2) Å and 2.29(2) Å, respectively, which are significantly shorter than those in the rubidium analogue. These short distances do not correspond to real bonds since they result from mixing the separate disordered models.

(19) (a) Brown, I. D.; Altermatt, D. *Acta Crystallogr.* **1985**, *B41*, 244. (b) Brese, N. E.; O'Keefe, M. *Acta Crystallogr.* **1991**, *B47*, 192.

(20) Nakamoto, K. In *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley and Sons: New York, 1986.

(21) Baran, E. J.; Pedregosa, J. C.; Aymonino, P. J. *J. Mol. Struct.* **1974**, *22*, 377.

(22) Harrison, W. T. A.; Liang, C. S.; Nenoff, T. M.; Stucky, G. D. *J. Solid State Chem.* **1994**, *113*, 376.

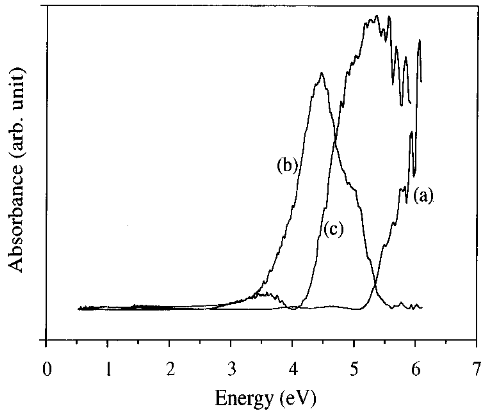

Figure 7. UV−vis spectra of (a) $RbNbAsO_5Cl$, (b) $CsNbAsO_5Cl$, and, for comparison, (c) β-$NbAsO_5$.

form of AsO_4 tetrahedra. The apical oxygen and chlorine atoms are connected to the alkali metal cation, A^+, i.e., Nb−O−A and Nb−Cl−A. Thus only one broad LMCT band due to AsO_4 LMCT is observed for both cases.

In summary, by employing the halide flux method we have successfully synthesized a new family of layered niobium(V) arsenate compounds $ANbAsO_5Cl$ (A = Rb, Cs). We have demonstrated that the formation of a layered structure can be derived if the $NbAsO_5$ framework is chemically dissected by molten alkali-metal chloride along the planes of long (weak) Nb−O bonds. This is, as far as we know, the first series of coordination-intercalated compounds by salt insertion. These studies further demonstrate the potential in the synthesis of new low-dimensional compounds by chemical dissection of extended solids containing weak linkages. The improved ionicity in the interlayer may extend the synthesis of inorganic/organic hybrid materials to less basic organic molecules.

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Supporting Information Available: Tables of detailed crystallographic data and anisotropic thermal parameters of $ANbAsO_5Cl$, positional parameters and selected bond distances of $CsNbAsO_5Cl$, powder X-ray diffraction patterns of aforementioned white, irregular shape particles, and bond valence sum calculations are available (11 pages). Ordering information is given on any current masthead page.

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