Inorg. Chem. **2003**, *42*, 7747–7751

Inorganic Chemistry

Article

$AVNb_3Cl_{11}$ (A = K, Rb, Cs, Tl): A Series of Layered Vanadium Niobium Halides Based on Triangular Nb_3 Clusters

Thirumalai Duraisamy and Abdessadek Lachgar*

Department of Chemistry, Wake Forest University, Winston-Salem, North Carolina 27109

Received February 11, 2003

The first quaternary vanadium niobium compounds containing triangular Nb_3 clusters corresponding to the general formula, $AVNb_3Cl_{11}$ (A = K, Rb, Cs, Tl), have been prepared in sealed quartz tubes from stoichiometric amounts of ACl (A = K, Rb, Cs), or Tl metal, VCl_3, Nb powder, and $NbCl_5$ heated at 740 °C. The compounds crystallize in the orthorhombic space group *Pnma* (No. 62). The crystal structures of the Rb and Tl members were determined by single-crystal X-ray diffraction techniques. Crystal data: $a = 12.771(3)$ Å, $b = 6.811(2)$ Å, $c = 17.183(3)$ Å, $V = 1494.6(1)$ Å^3, and $Z = 4$ for A = Rb; and $a = 12.698(5)$ Å, $b = 6.798(3)$ Å, $c = 17.145(10)$ Å, $V = 1480.0(13)$ Å^3, and $Z = 4$ for A = Tl. The crystal structure of $AVNb_3Cl_{11}$ consists of triangular Nb_3Cl_{13} clusters (Nb–Nb = 2.826 Å) connected to each other via four outer ligands to form infinite chains along the *b*-axis. The chains are connected by vanadium atoms located in an octahedral environment to form puckered sheets. The A^+ counterions are located between adjacent sheets and coordinate to twelve chlorine ligands in anticubeoctahedral geometry. Electronic structure calculations show bonding orbitals similar to those in Nb_3Cl_8. Magnetic susceptibility measurements show paramagnetic Curie Weiss behavior.

Introduction

Compounds containing triangular Nb_3 clusters have been extensively studied in recent years in the solid state and in solution.[1−3] The binary cluster compounds, Nb_3X_8 (X = Cl, Br, I) are based on $[Nb_3(\mu_3 - X^i)(\mu_2 - X^i)_3X^a_9]^{5-}$ cluster anion ((*i*) and (*a*) denote “inner” and “outer” ligand, respectively), formed of triangular Nb_3 metal core face-capped by one halogen ($\mu_3 - X$), edge-capped by three halogen ligands ($\mu_2 - X$), and nine other halogen ligands are located in apical positions.[4−6] The cluster units share all their outer ligands to form a layered structure according to the connectivity formula, $Nb_3(\mu_3-X^i)(\mu_2-X^i)_3X^{a-a}_{6/2}X^{a-a-a}_{3/3}$. Molecular orbital calculations have shown that in most Nb_3 cluster containing compounds the cluster is stable with six (e.g., Nb_3SBr_7,[7] Nb_3SI_7[8], and $(PEt_3H)[Nb_3Cl_{10}(PEt_3)_3$[9]]), seven (e.g., Nb_3X_8 (A = Cl, Br, I),[4−6] $CsNb_3SBr_7$[10]), or eight (e.g., $Nb_3Cl_7(PMe_2Ph)_6$[9]) valence electrons (VEC) available for metal−metal bonding. Modification of the cluster layers in Nb_3X_8 by either ligand substitution as is the case in the niobium chalcohalides Nb_3YX_7 (Y = chalcogen, X = halogen), which is based on $[Nb_3YX_{12}]^{5-}$ cluster units with six valence electrons, or stabilization of the Nb_3 units by countercations (e.g., pseudo-ternary series, ANb_3YX_7, where A = Rb, Cs; Y = chalcogen; X = halogen, which are based on $[Nb_3YX_{10}]^{4-}$ cluster units) led to the discovery of different structure types.[7,8,10,11]

Our work in this area focuses on the investigation of metal-rich halides and oxyhalides containing transition metals as counterions. In the chloride systems we reported the compounds $Rb_2Cu_2Nb_6Cl_{18}$,[12] $K_2MnNb_6Cl_{18}$,[13] the series $ATiNb_6Cl_{18}$ (A = K, Rb, Cs, In, Tl),[14] and $A_2VNb_6Cl_{18}$ (A = Tl, In,

---

* To whom correspondence should be addressed. E-mail: lachgar@wfu.edu. Phone: (336) 758 4676. Fax: (336) 758 4656.

(1) Müller, A.; Jostes, A.; Cotton, F. A. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 875.

(2) Millet, G. J. *J. Alloys Compd.* **1995**, *229*, 93.

(3) Kibala, E. B.; Cotton, F. A.; Shang, M. *Inorg. Chem.* **1990**, *29*, 5148.

(4) Von Schnering, H. G.; Wöhrle, H.; Schäfer, H. *Naturwissenschaften* **1961**, *48*, 159.

(5) Simon, A.; von Schnering, H. G. *J. Less-Common Met.* **1966**, *11*, 31.

(6) Ströbele, M.; Glaser, J.; Lachgar, A.; Meyer, H.-J. *Z. Anorg. Allg Chem.* **2001**, *627*, 2002.

(7) Khvorykh, G. V.; Shevelkov, A. V.; Dolgikh, V. A.; Popovkin, B. A. *J. Solid State Chem.* **1995**, *120*, 311.

(8) Schmidt, P. J.; Thiele, G. *Acta Crystallogr.* **1997**, *C53*, 1743.

(9) Cotton, F. A.; Diebold, M. P.; Feng, X.; Roth, W. J. *Inorg. Chem.* **1988**, *27*, 3413.

(10) Meyer, H.-J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 863.

(11) Miller, G. J.; Lin, J. *Angew Chem. Int. Ed. Engl.* **1994**, *33*, 334.

(12) Sitar, J.; Lachgar, A.; Meyer, H.-J. *Z. Kristallogr.* **1996**, *211*, 395.

(13) Sitar, J.; Lachgar, A.; Womelsdorf, H.; Meyer, H.-J. *J. Solid State Chem.* **1996**, *122*, 428.

(14) Nägele, A.; Anokhina, E. V.; Sitar, J.; Meyer, H.-J.; Lachgar, A. *Z. Naturforsch.* **2000**, *55b*, 139.

10.1021/ic0341439 CCC: $25.00

Rb),[15] which contain the octahedral $[Nb_6Cl_{18}]^{4-}$ units and Cu(I), Mn(II), Ti(III), and V(II) as counterions. In compounds containing triangular Nb_3 cluster units, only the pseudo ternary phases ANb_3YX_8 (A = Rb, Cs; Y = chalcogen; X = halogen) which contain the $[Nb_3YX_{10}]^{4-}$ unit have been reported. To date, no Nb_3 triangular cluster units have been isolated in the presence of transition metals as countercations. Transition-metal counterions can exhibit different coordination and different oxidation states, which may lead to stabilization of novel structures. In this paper we report the synthesis, crystal structure, magnetic properties, and electronic structures of the first quaternary niobium chloride cluster series containing triangular Nb_3 clusters and vanadium with the formula $AVNb_3Cl_{11}$ (A = K, Rb, Cs, Tl).

Experimental Section

Syntheses. $TlVNb_3Cl_{11}$ was initially formed as small black platelike crystals during our investigation of niobium oxychloride cluster compounds containing Tl and V as counterions. Subsequently, the series $AVNb_3Cl_{11}$ (A = K, Rb, Cs, Tl) was prepared quantitatively from reactions carried out using stoichiometric quantities of $NbCl_5$ (Alfa, 99.5%), Nb powder (Alfa 99.8%), VCl_3 (Alfa 99.8%), and KCl (Alfa, 99.99%) or RbCl (Alfa, 99.99%) or CsCl (Alfa, 99.9%) or Tl metal (Johnson Matthey, 99.99%). The mixtures were handled under argon atmosphere, sealed in silica tubes (length 4 cm, i.d.7 mm) under vacuum, heated at 740 °C for one week, followed by slow cooling to 550 °C in 48 h and radiative cooling to room temperature. The products were obtained as black, air-stable platelike crystals between 0.15 and 0.3 mm in size.

Elemental Analysis. The products were analyzed by X-ray microanalysis (EDAX). The spectra were obtained with a Philips 515 scanning electron microscope equipped with an EDAX microprobe, at an accelerating voltage of 30 kV, beam diameter of 50−100 μm, and counting times of 50−100 s. The analysis confirmed the presence of alkali metals or Tl, and V, Nb, and Cl.

Phase Analysis. The products were characterized by X-ray powder diffraction for phase purity. Powder patterns were recorded on an automated Philips diffractometer using Cu Kα radiation. The phases $RbVNb_3Cl_{11}$ and $TlVNb_3Cl_{11}$ were obtained in yields >90% with $Tl_2VNb_6Cl_{18}$[15] as the only minor product observed in XPD. In the reactions of K and Cs, ca. 50% Nb_3Cl_8 was observed.

Magnetic Measurements. Magnetic susceptibility measurements as a function of temperature (2−300 K) were carried out using a Quantum Design MPMS XL SQUID magnetometer. Loose crystals (54.4 mg) of the thallium phase were manually selected and placed into a gelatin capsule, which was placed inside a plastic straw. Samples were measured under both zero-field-cooled (zfc) and field-cooled (fc) conditions. In both cases, the magnetization was measured in the temperature range 2−300 K at applied fields of 5 and 10 kG. In addition, fields sweep at applied fields between −40 kG and 40 kG was measured at 5 K. The very small diamagnetic contribution of the gelatin capsule containing the sample had a negligible contribution to the overall magnetization, which was dominated by the sample signal.

Electronic Structure Calculations. Electronic structure calculations were carried out using the extended-Hückel tight-binding method.[16−18] The density of states (DOS) were calculated using a set of 24 special k-points uniformly distributed over the asymmetric unit of the Brillouin Zone, and a set of 88 k-points was used to verify the convergence. The calculations were carried out on $[VNb_3Cl_{11}]^-$, $[Nb_3Cl_{11}]^{n-}$ (n = 3, 4), and $[Nb_3Cl_{13}]^{n-}$ anions, and on the entire structure, $AVNb_3Cl_{11}$. Niobium atomic orbital energies were corrected for charge transfer,[19] and these parameters together with those for V and Cl are available as Supporting Information.

Table 1. Crystal Data and Structural Refinement Parameters for $AVNb_3Cl_{11}$ (A = Rb, Tl)

	A = Rb	A= Tl
chemical formula	$RbVNb_3Cl_{11}$	$TlVNb_3C_{l1}$
FW	805.09	923.99
temperature (K)	293(2)	228(2)
wavelength (Å)	0.71073	0.71073
space group	*Pnma* (No. 62)	*Pnma* (No. 62)
a (Å)	12.771(3)	12.698(5)
b (Å)	6.8110(17)	6.798(3)
c (Å)	17.183(3)	17.145(10)
V (Å^3)	1494.6(6)	1480.0(13)
Z	4	4
ρ_{calcd} (g/cm^3)	3.578	4.147
μ (cm$^{-1)}$	80.1	156.6
$R_1/wR_2{}^a$ (all data)	0.067/0.121	0.076//0.178

[a] $R_1 = (||F_o| - |F_c||)/(|F_o|)$; $wR_2 = [(w(F_o{}^2 - F_c{}^2)/(wF_o{}^4)^{1/2}$.

Crystal Structure Determination of $RbVNb_3Cl_{11}$. A suitable single crystal of 0.2 × 0.2 × 0.10 mm^3 was selected and mounted in a glass capillary for X-ray diffraction analysis. Intensity data were collected at 293(2) K on a Bruker P4 X-ray diffractometer using Mo Kα radiation. The unit cell parameters were refined using 51 centered reflections to give an orthorhombic unit cell with lattice parameters $a = 12.771(3)$, $b = 6.811(2)$, and $c = 17.183(3)$ Å. A total of 2464 reflections was collected ($2.37° < \theta < 27.49$) of which 1847 were unique. An empirical ψ scan absorption correction based on 10 reflections was applied. Extinction conditions and Laue symmetry suggested *Pnma* or *Pna2*(1) as possible space groups. The structure was solved in *Pnma* as intensity statistics indicated a centrosymmetric space group. Initial atomic positions of all atoms were determined using direct methods.[20] Least-squares refinement (Shelxl-93) of a model containing all atoms with isotropic thermal parameters converged to $R_1 = 0.0731$ and $wR_2 = 0.1758$ for all data.[21] Subsequent refinement with anisotropic thermal parameters converged to $R_1 = 0.0671$ and $wR_2 = 0.1214$ for all data. Refinement of the structure in the noncentrosymmetric space group *Pna2₁* did not lead to any statistically significant differences. Further details regarding data collection and refinement parameters are listed in Table 1. Positional and equivalent isotropic thermal parameters, and anisotropic displacement parameters for Rb and Tl phases are submitted as Supporting Information in CIF format.

The unit cell parameters for the compounds $AVNb_3Cl_{11}$ (A = K, Cs) were determined from single-crystal X-ray diffraction studies. For A = K: $a = 12.652(1)$ Å, $b = 6.701(1)$ Å, $c = 17.055(1)$ Å, and $V = 1445.93$ Å^3. For A = Cs: $a = 12.659(7)$ Å, $b = 6.783(3)$ Å, $c = 17.091(10)$ Å, and $V = 1467.45$ Å^3.

---

(15) Duraisamy, T.; Qualls, J. S.; Lachgar, A. *J. Solid State Chem.* **2003**, *170*, 227.

(16) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(17) Hoffmann, R. *Solids and Surfaces: A Chemists View of Bonding in Extended Structures*; VCH Publishers: New York, 1988, and references therein.

(18) Whangbo, M.-H.; Evain, M.; Hughbanks, T.; Kertesz, M.; Wijeyesekera, S,; Wilker, C.; Zheng, C.; Hoffmann, R. *Extended-Huckel Molecular, Crystal, and Properties Package*; Quantum Chemical Program Exchange, 1989.

(19) Baranovskii, V. I.; Nikolskii, A. B. *Teor. Eksp. Khim.* **1967**, *3*, 527.

(20) Sheldrick, G. M. *SHELXS-97, Program for Structure Solution;* University of Göttingen: Germany.

(21) Sheldrick, G. M. *SHELXL-97, Program for Structure Refinement,* University of Göttingen: Germany.

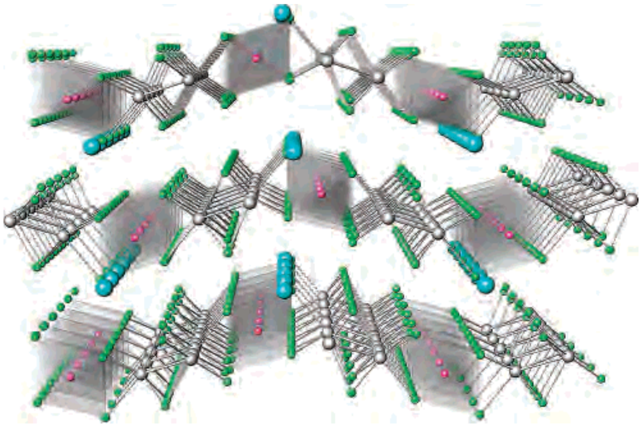

Figure 1. Perspective view of the crystal structure of $AVNb_3Cl_{11}$ showing the puckered layers stacked along the crystallographic *a* axis. Vanadium coordination is shown as polyhedral representation: Nb, gray; Cl, green; V, red; A, blue.

Table 2. Selected Bond Lengths [Å] and Angles [°] for $AVNb_3Cl_{11}$

	A = Rb	A = Tl
Nb(1)−Nb(1)	2.833(2)	2.828(3)
Nb(1)−Nb(2)	2.8187(17)	2.824(2)
Nb(1)−Cl(1)	2.445(4)	2.436(4)
Nb(1)−Cl(2)	2.439(4)	2.427(3)
Nb(1)−Cl(3)	2.551(3)	2.553(3)
Nb(1)−Cl(5)	2.440(4)	2.428(4)
Nb(1)−Cl(6)	2.506(3)	2.516(3)
Nb(1)−Cl(7)	2.638(3)	2.641(3)
Nb(2)−Cl(4) × 2	2.524(3)	2.522(3)
Nb(2)−Cl(5)	2.450(5)	2.442(5)
Nb(2)−Cl(6) × 2	2.428(3)	2.423(3)
Nb(2)−Cl(8)	2.603(5)	2.598(5)
V−Cl(4)	2.461(6)	2.467(6)
V−Cl(6) × 2	2.464(4)	2.460(4)
V−Cl(7)	2.485(5)	2.469(6)
V−Cl(8) × 2	2.490(4)	2.483(4)
A−Cl	3.4337(11)−3.690(5)	3.322(1)−3.819(1)
V−Nb	3.265(1)−3.731(1)	3.252(2)−3.719(2)
Nb(2)−Nb(1)-Nb(1)	59.84(3)	59.95(3)
Nb(1)−Nb(2)-Nb(1)	60.33(6)	60.10(7)
Nb(2)−Cl(6)-Nb(1)	70.79(10)	70.99(14)
Nb(1)−Cl(5)-Nb(1)	70.80(13)	70.88(13)

Results and Discussion

The series $AVNb_3Cl_{11}$ crystallizes in the orthorhombic space group, *Pnma*, and is based on triangular Nb_3Cl_{13} cluster units, linked through four outer chlorine ligands (Cl^{a-a}) to form chains that are connected to each other through vanadium cations to form puckered sheets. The overall structure of the compound $RbVNb_3Cl_{11}$ is given in Figure 1.

The Nb_3Cl_{13} cluster unit consists of three $NbCl_6$ octahedra each of which shares a pair of Cl^i edges, one vertex being common to all three, and nine other Cl^a ligands in apical positions, viz., $Nb_3Cl^i_{3/3}Cl^i_{6/2}Cl^a_9$. The intra-cluster bonding parameters are given in Table 2. The observed bonding parameters of the cluster unit $d(Nb-Nb) = 2.819(1) - 2.833(2)$, $d(Nb-(\mu_2-Cl)^i) = 2.428(3) - 2.445(4)$, $d(Nb-(\mu_3-Cl)^i) = 2.440(4) - 2.450(5)$ and $d(Nb-Cl^a) = 2.505(3) - 2.638(3)$ Å are similar to those found in other cluster compounds containing triangular Nb_3Cl_{13} units.[1-4,6,22] The average $d(Nb-Nb)$ distance, 2.826(1) Å is between that found in Nb_3Cl_8[6,22] with VEC = 7 ($d(Nb-Nb) = 2.808(1)$ Å) and that found in $Nb_3Cl_7(PMe_2Ph)_6$[9] ($d(Nb-Nb) = 2.832(1)$ Å) which has VEC = 8. In contrast, significantly longer Nb−Nb distances have been reported for six-electron Nb_3 clusters (e.g., Nb−Nb = 2.976(1) Å, in $(HPEt_3)Nb_3Cl_{10}(PEt_3)_3$[9]).

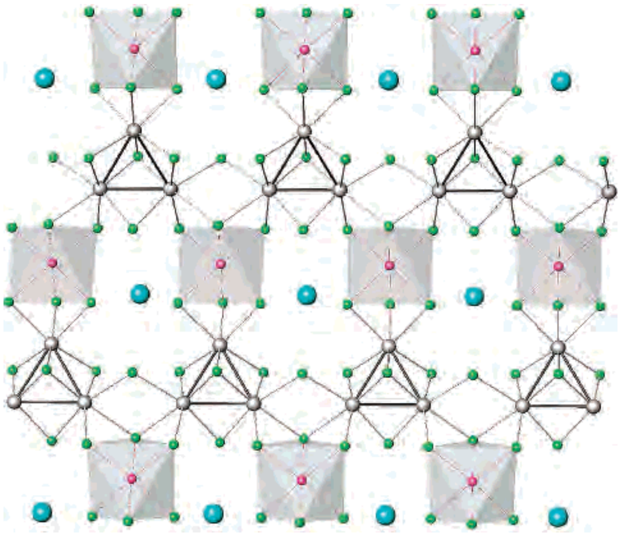

Figure 2. Projection of a layer in $AVNb_3Cl_{11}$ showing cluster connectivity into chains and the vanadium octahedra linking the chains to form layers.

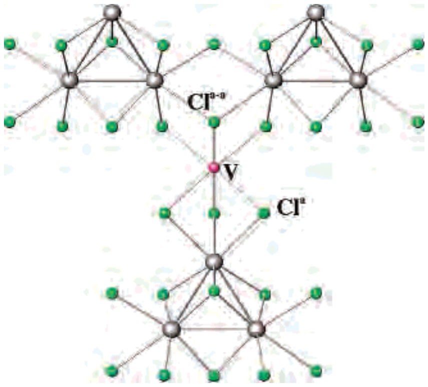

Figure 3. View of the octahedral coordination environment of vanadium formed of five Cl^a and one Cl^{a-a} ligands from three neighboring Nb_3Cl_{13} units.

The Nb_3Cl_{13} units share four Cl^{a-a} atoms to form infinite chains running along the *b*-axis, according to the connectivity formula, $Nb_3(\mu_3 - Cl^i)(\mu_2 - Cl^i)_3Cl^a{}_5Cl^{a-a}{}_{4/2}$ (Figure 2). One bridging ligand, Cl^{a-a} and the five remaining terminal Cl^a coordinate to the vanadium atoms which join the chains into puckered sheets that stack along the *a*-axis. The μ_3-Cl^i and the bridging Cl^{a-a} coordinate to three niobium, and two niobium and one vanadium, respectively, and all other chloride ligands are bonded to either two niobium, or one niobium and one vanadium atoms. The chains occur with alternate orientations of the capping μ_3-Cl^i ligand.

Puckering within the layers results from alternate rotations of adjoining chains, approximately by 19° about the Nb−Nb edges of the Nb_3 cluster, so as to generate suitable coordination sites for the vanadium atoms (Figure 3). Five Cl^a and one Cl^{a-a} ligands from three neighboring cluster units in two adjacent layers coordinate the vanadium. The average

---

[22] Miller, G. J. *J. Alloys Compd.* **1995**, *217*, 5.

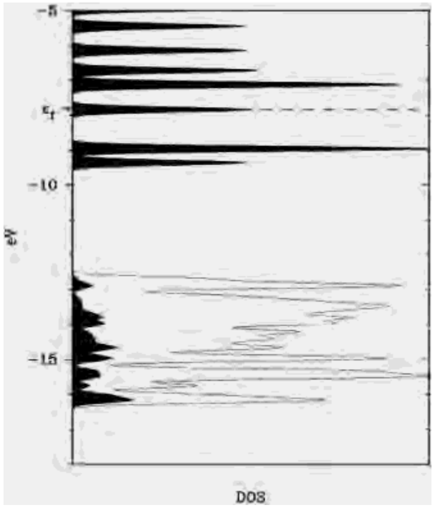

Figure 4. Density of states (DOS) for $[Nb_3Cl_{11}]^{4-}$. The Nb contribution is shaded in black and the Fermi level is marked as a dotted line

d(V−Cl) = 2.475(6) Å, is between the V−Cl distances in binary vanadium chlorides, VCl_2 (V−Cl = 2.539(1) Å)[23] and VCl_3(V−Cl = 2.417(5) Å),[24] indicating that the vanadium could be present in mixed valence with a formal oxidation state $V^{+2.5}$. The oxidation state of vanadium is confirmed based on bond valence sums:[25] BVS for average d(V−Cl), 0.409 × 6 = 2.456(1). The Rb^+ cations occupy distorted anticubeoctahedral sites between the layers, holding the layers together into three dimensions, and are coordinated by 12 chlorine ligands. The average d(Rb−Cl) distance 3.569(4) Å (Table 2) is in good agreement with the sum of the ionic radii of the Rb^+ (1.72 Å, CN = 12) and Cl^- (1.81 Å) ions.[26]

Several molecular orbital (MO) calculations have been performed on the $(Nb_3X_{13})^{5-}$ anion and Nb_3X_8 compounds.[19,27−31] There are nine molecular orbitals, of which four are in the metal−metal bonding states, which indicates that the Nb_3 cluster can be stabilized with a maximum of eight electrons. In the $(Nb_3X_{13})^{5-}$ unit, six electrons occupy the most strongly bonding Nb−Nb states, $1a_1$ and 1e, and the weakly bonding $2a_1$ level accommodates the seventh electron which is half filled in the case of Nb_3Cl_8 (VEC = 7), and fully occupied in eight electron systems.[9] The density of states (DOS) for the Nb_3 cluster of the title phase in the energy region −18.0 to −5.0 eV covering the Fermi level is shown in Figure 4.

The position of the Fermi level lies on the DOS peak that is essentially of $2a_1$ character located at −7.85 eV. The energy bands at −9.41 eV ($1a_1$ level), −9.06 eV (1e level) and −7.85 eV ($2a_1$ level) correspond to Nb−Nb bonding states. The broad bands below −12.5 eV are primarily chloride states lying at lower energy than the higher occupied orbitals of mostly niobium character. The lowest lying Nb−Nb states are located at lower energies compared to Nb_3Cl_8, indicating an increase in bonding character. However, the Nb−Nb bonding scheme is still much the same. A similar trend has been observed between six- and eight-electron molecular cluster compounds, $(HPEt_3)Nb_3Cl_{10}(PEt_3)_6$ and $Nb_3Cl_7(PEt_3)_6$.[9] The intermediate state between seven and eight valence electrons does not lead to any significant change in the electronic structures.

Magnetic susceptibility measurements performed on $TlVNb_3Cl_{11}$ bulk crystalline sample between 2 and 300 K show paramagnetic Curie−Weiss behavior ($C = 1.47$ emu K mol^{-1}, $\theta = -6.44$ K, and $\chi_{TIP} = 4.68 \times 10^{-4}$ emu mol^{-1}) with an effective magnetic moment of 3.43 μ_B per formula unit, which is close to the expected value for 2.5 unpaired electrons (3.35 μ_B) from one $V^{2.5+}$ per formula unit. These measurements, along with results from bond valence calculations and the extended-Hückel calculations, indicate that the number of valence electrons per Nb_3 cluster could be 7.5.

Conclusion

The structure of the title compound is the first example of a layered material based on triangular Nb_3Cl_{13} cluster units and vanadium. The compound is isostructural with KTi_4Cl_{11}[32] in which infinite chains, $[Ti_3(\mu_3 - Cl^i)(\mu_2 - Cl^i)_3Cl^a{}_5Cl^{a-a}{}_{4/2}]^1{}_\infty$ built of Ti_3Cl_{13} cluster units, are linked by Ti(IV) to form sheets. The puckered layers in the structure of $AVNb_3Cl_{11}$ appear to be similar to the wavelike nets found in ANb_4Cl_{11} (A = Rb, Cs)[33,34] in which the $[Nb_4Cl_{16}]^{6-}$ cluster units compose the layers according to the connectivity formula $Nb_4Cl^i{}_6Cl^a{}_{10/2.}$ However, the cluster framework in the title phases consists of infinite chains made of $Nb_3Cl_4Cl^a{}_5Cl^a{}_{4/2}$ units. Vanadium is present in mixed valence state with formal oxidation state, $V^{+2.5}$, and consequently, the valence electrons available for Nb−Nb bonding is 7.5. The mixed valence vanadium is consistent with the magnetic susceptibility data, the V−Cl bond lengths, and bond valence sum calculations. Extended-Hückel calculations show that the electronic structure of the cluster anion $[Nb_3Cl_4Cl_5Cl_{4/2}]^{5-}$ in the title phase is similar to that of the $[Nb_3Cl_4Cl_{3/3}Cl_{6/2}]^{5-}$ subunits in Nb_3Cl_8 with seven valence electrons, and to that of the molecular cluster unit $[Nb_3Cl_7]$ in $[Nb_3Cl_7(PEt_3)_3]$, with eight electrons, except for a small increase in Nb−Nb bonding character ($2a_1$ level) compared to Nb_3Cl_8. The observed d(Nb−Nb) = 2.808(1) Å in Nb_3Cl_8 is comparatively shorter than that found in the title compound (average d(Nb−Nb) = 2.826(1) Å) which could be explained by constraints specific to the 2D structure of Nb_3Cl_8.

Acknowledgment. We thank the National Science Foundation, which supported this work through Grant

---

(23) Villard, J. *Acta Chem. Scand.* **1959**, *13*, 244.
(24) Klemm, W.; Krose, E. *Z Anorg. Allg. Chem.* **1947**, *253*, 218.
(25) O'Keeffe, M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 3226.
(26) Shannon, R. D. *Acta Crystallogr.* **1976**, *A32*, 751.
(27) Cotton, F. A.; Hass, T. E. *Inorg. Chem.* **1964**, *3*, 10.
(28) Bursten, B. E.; Cotton, F. A.; Stanley, G. G. *Isr. J. Chem.* **1982**, *19*, 132.
(29) Bursten, B. E.; Cotton, F. A.; Hall, M. B.; Najjar, R. *Inorg. Chem.* **1982**, *21*, 302.
(30) Meyer, H.-J. *Z. Anorg. Allg. Chem.* **1994**, *620*, 81.
(31) Kennedy, J. R.; Adler, P.; Dronskowski, R.; Simon, A. *Inorg. Chem.* **1996**, *35*, 2276.
(32) Zhang, J.; Qi, R.-Y.; Corbett, J. D. *Inorg. Chem.* **1991**, *30*, 4794.
(33) Broll, A.; Simon, A.; von Schnering, H.-G.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1969**, *367*, 1.
(34) Ströbele, M.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **2002**, *628*, 1022.

DMR0070915. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society ACS-PRF#36080-AC5 for partial support of this work. We also thank Katie Stitzer and Prof. Hanno zur Loye, University of South Carolina, for the magnetic data measurements.

Supporting Information Available: One X-ray crystallographic file containing data for $AVNb_3Cl_{11}$ (A = Rb, Tl) (CIF); table of parameters used in electron structure calculations and a plot of the magnetic susceptibility data (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

IC0341439