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Journal of Solid State Chemistry 170 (2003) 227–231

JOURNAL OF
SOLID STATE
CHEMISTRY

<http://elsevier.com/locate/jssc>

$A_2VNb_6Cl_{18}$ ($A = Rb, In, Tl$): synthesis, crystal structure and magnetic properties of a new series of quaternary niobium chloride cluster compounds

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Received 5 March 2002; received in revised form 12 September 2002; accepted 25 September 2002

Abstract

A new series of quaternary niobium chloride cluster compounds corresponding to the general formula, $A_2VNb_6Cl_{18}$ ($A = Rb, Tl$ or In), has been prepared in sealed quartz tubes from a mixture containing $NbCl_5$, Nb , VCl_3 and $RbCl$, or In or Tl metal by solid state reactions at $750^\circ C$. The structure of $Tl_2VNb_6Cl_{18}$ was determined using single-crystal X-ray diffraction: Crystal data: rhombohedral, $R\bar{3}$ (No. 148), $a = 9.1122(17)$, $c = 25.178(7)$ Å, $V = 1810.5(7)$ Å³ and $Z = 3$. The full-matrix least-squares refinement against F^2 converged to $R_1 = 0.0515$, $wR_2 = 0.1104$ (all data). The structure consists of discrete octahedral cluster units, $[Nb_6Cl_{12}Cl_6]^{4-}$ linked by V^{2+} and A^+ cations, located in a 6-coordinated octahedral and 12-coordinated anticeuboctahedral chloride environment, respectively. The intra-cluster bond lengths indicate 16 valence electrons per cluster. Magnetic susceptibility studies show paramagnetic behavior with a magnetic moment of $3.37 \mu_B$ per formula unit. Electrical resistivity measurements indicate a semiconducting behavior.

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Keywords: Cluster; Crystal structure; Magnetic properties; Niobium; Chloride; Vanadium

1. Introduction

Investigations of metal-rich niobium halides containing Nb_6 octahedral clusters led to the discovery of a number of original structure types in which the $[Nb_6X_{18}]^{n-}$ ($X = Cl$ or Br) anionic cluster constitutes the basic building block [1–4]. In most compounds obtained through solid-state high-temperature synthesis the cluster unit is stable with 16 valence electrons (VEC) available for metal–metal bonding. The anionic cluster unit can be stabilized using a combination of (+1) metal cations as in $K_4Nb_6Cl_{18}$ [5], $A_2Li_2Nb_6Cl_{18}$ ($A = In$ or Tl) [6] and $K_2SrNb_6Cl_{18}$ [7]. Perrin et al. prepared a number of niobium chloride cluster compounds corresponding to the general formula $A_xLnNb_6Cl_{18}$ ($A = alkali$ and $Ln = lanthanide$) ($x = 0, 1, 2$) [8–11], wherein the $[Nb_6Cl_{18}]^{4-}$ anionic chloride units are stabilized by a combination of lanthanide and monovalent metal

cations. These compounds crystallize in the rhombohedral crystal system (space group $R\bar{3}$) except for $CsLnNb_6Cl_{18}$, which crystallizes in the trigonal crystal system (space group $P\bar{3}1c$). The series $LnNb_6Cl_{18}$ [9,11] is based on cluster units containing 15 electrons in metal–metal bonding states leading to paramagnetic behavior. Our work in this field has focused on the investigation of halides and oxyhalides containing transition metals as counter-ions and led to the discovery of $Rb_2Cu_2Nb_6Cl_{18}$ [12] which contains $Cu(I)$, $K_2MnNb_6Cl_{18}$ [13] which contains $Mn(II)$, the series $ATiNb_6Cl_{18}$ ($A = K, Rb, Cs, In, Tl$) [14], which contains $Ti(III)$ and a number of low-dimensional oxychlorides containing $Ti(III)$ as counter-ion [15–19]. In this paper, we report the synthesis of the new reduced niobium chloride cluster compound series with the general formula $A_2VNb_6Cl_{18}$ ($A = Rb, Tl$ or In) containing vanadium counter-cations and alkali metals or group 13 cations. The crystal structure of $Tl_2VNb_6Cl_{18}$ and its magnetic properties are discussed.

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2. Experimental

2.1. Syntheses

Tl₂VNb₆Cl₁₈ was initially formed as black shiny cuboctahedral crystals from a reaction proposed to yield an oxychloride compound of the composition, TlV₂Nb₆Cl₁₀O₆. The series A₂VNb₆Cl₁₈ (A = Rb, Tl or In) was then, prepared quantitatively from reactions carried out using stoichiometric quantities of NbCl₅ (Alfa, 99.5%), Nb powder (Alfa 99.8%), VCl₃ (Alfa 99.8%), and Tl (Johnson Matthey, 99.999%) or RbCl (Alfa, 99.99%) or In metal (Johnson Matthey, 99.9%). The mixtures were handled under argon atmosphere and the reactions were performed in sealed quartz tubes at 750°C for 4 days. The heating and cooling ramps were 25°C/h and 20°C/h, respectively. The products were obtained as shiny black (dark green when ground) air stable crystals between 0.1 and 0.4 mm in size. The compounds are soluble in water and ethanol giving intense green colored solutions indicating the characteristic color of 16-electron niobium halide clusters [20–22].

The products were analyzed by X-ray powder diffraction (CuKα) for phase purity. All phases were obtained in yields ≈90% with NbOCl₂ as the only impurity observed in XRD. Crystals of the new phases were analyzed for elemental composition using EDAX. The spectra were obtained using a Philips 515 scanning electron microscope equipped with a microprobe.

2.2. Magnetic measurements

Magnetic susceptibility measurements as a function of temperature (2–300 K) were carried out at 0.5 and 4 T, using a quantum design MPMS superconducting quantum interference device (SQUID) magnetometer. The bulk-crystalline sample (25.5 mg) was contained in a gel capsule fixed inside a plastic straw for immersion into the SQUID. No diamagnetic correction was made for the sample container because its signal was not significant relative to that of the sample.

2.3. Electrical resistivity properties

The electrical resistivity was measured in the temperature range 150–300 K using two-probe technique due to high resistivity values in the temperature range studied. Leads were attached on a single crystal of size 0.2 × 0.2 × 0.2 mm³ using carbon XC-12 conductive paint, and the contact between the material and the leads was ohmic.

2.4. Crystal structure determination

A suitable crystal of size 0.15 × 0.15 × 0.15 mm³ was selected and mounted in a glass capillary for X-ray

diffraction analysis. Intensity data were collected at 218(2) K on a Bruker P4 X-ray diffractometer using MoKα radiation. The unit cell parameters were refined using 44 centered reflections to give a rhombohedral cell with lattice parameters $a = 9.1122(17)$, $c = 25.178(7)$ Å. A full sphere of data was collected in the theta range, $2.70^\circ < \theta < 34.10^\circ$. A total of 3135 reflections were collected of which 1443 were unique. An empirical ψ scan absorption correction based on 12 reflections was applied. Extinction conditions and Laue symmetry suggested $R\bar{3}$ and $R\bar{3}$ as possible space groups. The structure was solved in $R\bar{3}$ as intensity statistics indicated a centrosymmetric space group. Initial atomic positions of all atoms were determined using direct methods (Shelxs-86). Least-squares refinement (Shelxl-93) of a model containing all atoms with isotropic thermal parameters converged to $R_1 = 0.0663$ and $wR_2 = 0.1683$ for all data. Subsequent refinement with anisotropic thermal parameters converged to $R_1 = 0.0515$ and $wR_2 = 0.1104$ for all data. Refinement of the structure in the non-centrosymmetric space group, $R3$ did not lead to any significantly different features. Further details regarding data collection and refinement parameters, and positional and equivalent isotropic thermal parameters are listed in Tables 1 and 2, respectively. The unit cell parameters for the compounds A₂VNb₆Cl₁₈ (A = Rb or In) were determined from single-crystal X-ray diffraction studies: For A = Rb: $a = 9.1226(6)$, $c = 25.1660(3)$ Å and $V = 1813.8(1)$ Å³; for A = In: $a = 9.128(8)$, $c = 25.176(3)$ Å and $V = 1816.9(3)$ Å³.

Table 1
Crystallographic data and experimental details of Tl₂VNb₆Cl₁₈

Empirical formula	Tl ₂ VNb ₆ Cl ₁₈
Formula weight (g)	1655.24
Temperature (K)	218(2)
Wavelength (Å)	0.71073
Crystal system	Rhombohedral
Space group	$R\bar{3}$ (148)
a (Å)	9.1122(17)
c (Å)	25.178(7)
V (Å ³)	1810.5(7)
Z	3
ρ (g/cm ³)	4.554
θ range (°)	2.7–34.10
$F(000)$	2211
Independent reflections	1443 [$R_{\text{int}} = 0.0285$]
Absorption coefficient (mm ⁻¹)	18.39
GOF ^a	1.104
$R_1/wR_2 [I > 2\sigma(I)]^a$	0.0432/0.1068
R_1/wR_2 (all data)	0.0515/0.1104

^a $R_1 = (||F_o|| - |F_c|)/||F_o||$; $wR_2 = [(w(F_o^2 - F_c^2))/(wF_o^4)]^{1/2}$; $GOF = [(w(F_o^2 - F_c^2)^2)/(n - p)]^{1/2}$, where 'n' is the number of reflections and 'p' is the number of parameters refined.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for $\text{Tl}_2\text{VNb}_6\text{Cl}_{18}$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Nb	0.53709(6)	0.82637(6)	0.119119(18)	0.00568(13)
Tl	0.6667	0.3333	0.05557(2)	0.02778(17)
V	0.0000	0.0000	0.0000	0.0046(3)
Cl(1)	0.38412(16)	0.90455(16)	0.05508(5)	0.0098(2)
Cl(2)	0.61995(16)	1.09233(16)	0.16597(5)	0.0093(2)
Cl(3)	0.79024(16)	1.03194(17)	0.05790(5)	0.0101(2)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3. Results and discussion

$\text{Tl}_2\text{VNb}_6\text{Cl}_{18}$ crystallizes in the rhombohedral space group, $R\bar{3}$; the structure is based on cluster anions, $[(\text{Nb}_6\text{Cl}_{12}^i)\text{Cl}_6^{\text{a}}]^{4-}$ linked through Tl and V atoms. The cluster anion, $[(\text{Nb}_6\text{Cl}_{12}^i)\text{Cl}_6^{\text{a}}]^{4-}$ (where (i) and (a) denote ‘inner’ and ‘outer’ ligands, respectively) consists of Nb_6 octahedron in which all edges are bridged by chloride ligands, and six other chloride ligands are in apical positions (Fig. 1). The intra-cluster bonding distances are given in Table 3: $\text{Nb-Nb} = 2.931(1)–2.932(1)$, $\text{Nb-Cl}^i = 2.445(1)–2.458(1)$ and $\text{Nb-Cl}^{\text{a}} = 2.624(1)$ Å are typical for compounds containing octahedral $[\text{Nb}_6\text{Cl}_{18}]^{4-}$ clusters. The observed Nb-Nb and Nb-Cl^i bond distances clearly indicate that the number of electrons available for metal–metal bonding (the so-called valence electrons per cluster (VEC)) is 16, as is the case for most other niobium chloride cluster compounds (e.g. $\text{Nb-Nb} = 2.915$, $\text{Nb-Cl}^i = 2.445$ and $\text{Nb-Cl}^{\text{a}} = 2.667$ Å in $\text{CsLuNb}_6\text{Cl}_{18}$ (10), $\text{Nb-Nb} = 2.927$, $\text{Nb-Cl}^i = 2.455$ and $\text{Nb-Cl}^{\text{a}} = 2.598$ Å in $\text{K}_2\text{SrNb}_6\text{Cl}_{18}$ (7), and $\text{Nb-Nb} = 2.932$, $\text{Nb-Cl}^i = 2.455$ and $\text{Nb-Cl}^{\text{a}} = 2.615$ Å in $\text{K}_2\text{MnNb}_6\text{Cl}_{18}$ [13]). The difference in the Nb-Cl^{a} distance of these compounds could be explained by the difference in the charge of the counter-cations and the difference in their ionic radii. In contrast, significantly longer Nb-Nb and shorter Nb-Cl^i distances have been reported for 15 electron Nb_6 clusters: e.g. $\text{LuNb}_6\text{Cl}_{18}$ ($\text{Nb-Nb} = 2.96$ Å, $\text{Nb-Cl}^i = 2.43$ Å) [9] and $[(\text{CH}_3)_4\text{N}]_3\text{Nb}_6\text{Cl}_{18}$ ($\text{Nb-Nb} = 2.97$ Å, $\text{Nb-Cl}^i = 2.43$ Å) [23].

The three-dimensional structure of the compound can be described on the basis of the anionic $[(\text{Nb}_6\text{Cl}_{12}^i)\text{Cl}_6^{\text{a}}]^{4-}$ cluster units linked through Tl^+ and V^{2+} cations to form cluster layers stacked along the *c*-axis (Fig. 2). Each cluster layer consists of three close packed layers of chloride ions in which one of every seven sites is vacant. The Tl^+ cations fully occupy distorted antioctahedral sites in the structure, and are coordinated to 12 chlorine ligands (Fig. 3a). The average Tl-Cl bond distance 3.44 Å (Table 3) is in good agreement with the sum of the ionic radii of the Tl^+ (1.70 Å, CN = 12) and

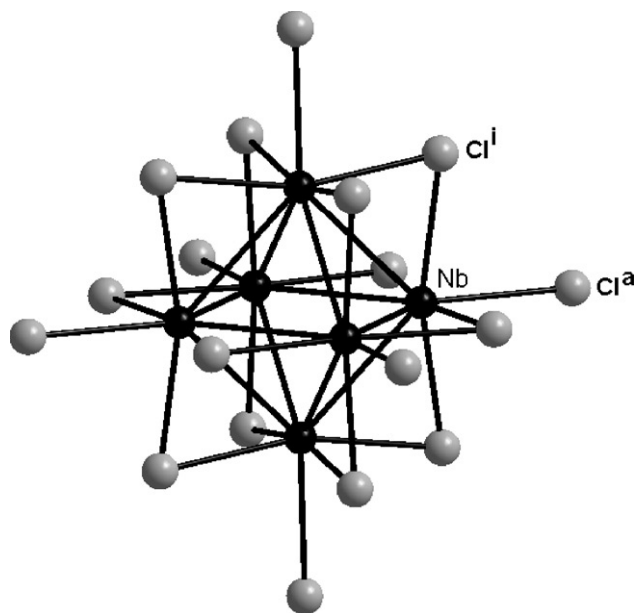


Fig. 1. Niobium chloride cluster anion, $[(\text{Nb}_6\text{Cl}_{12}^i)\text{Cl}_6^{\text{a}}]^{4-}$ present in $\text{Tl}_2\text{VNb}_6\text{Cl}_{18}$ (i) and (a) denote inner and outer ligands, respectively).

Table 3
Selected bond distances (Å) and angles ($^\circ$) for $\text{Tl}_2\text{VNb}_6\text{Cl}_{18}$

$\text{Nb-Nb}^{\text{a}} 2 \times$	2.932(1)
$\text{Nb-Nb}^{\text{b}} 2 \times$	2.931(1)
$\text{Nb-Cl}(1)$	2.458(1)
$\text{Nb-Cl}(1)^{\text{b}}$	2.452(1)
$\text{Nb-Cl}(2)$	2.451(1)
$\text{Nb-Cl}(2)^{\text{a}}$	2.445(1)
$\text{Nb-Cl}(3)$	2.624(1)
$\text{V-Cl}(3) 6 \times$	2.534(1)
$\text{Tl}(1)-\text{Cl}(1) 3 \times$	3.440(2)
$\text{Tl}(1)-\text{Cl}(1)^{\text{b}} 3 \times$	3.436(2)
$\text{Tl}(1)-\text{Cl}(2) 3 \times$	3.434(1)
$\text{Tl}(1)-\text{Cl}(3) 3 \times$	3.451(1)
$\text{Nb}^{\text{a}}-\text{Nb}-\text{Nb}^{\text{c}}$	90.0
$\text{Nb}^{\text{a}}-\text{Nb}-\text{Nb}^{\text{d}}$	59.97(3)
$\text{Nb}^{\text{c}}-\text{Nb}-\text{Nb}^{\text{d}}$	60.014(13)
$\text{Nb}^{\text{d}}-\text{Cl}(1)-\text{Nb}$	73.57(4)
$\text{Nb}^{\text{c}}-\text{Cl}(2)-\text{Nb}$	73.29(4)

Symmetry transformations used to generate equivalent atoms:

$$^{\text{a}} y - 1/3, -x + y + 1/3, -z + 1/3.$$

$$^{\text{b}} -x + y, -x + 1, z.$$

$$^{\text{c}} -y + 1, x - y + 1, z;$$

$$^{\text{d}} x - y + 2/3, x + 1/3, -z + 1/3.$$

Cl^- (1.81 Å) ions [24]. The vanadium is located between the cluster layers, and is coordinated by six apical chlorine ligands ($\text{Cl}(3)$) from six neighboring cluster units, to form a regular VCl_6 octahedron (Fig. 3b). The V-Cl distance, 2.534(1) Å, compares well with the reported V-Cl distances of binary vanadium chloride,

VCl_2 ($\text{V}-\text{Cl}=2.539(1)\text{\AA}$) [25], indicating that the vanadium is present as V^{2+} . The $\text{V}-\text{Cl}$ distance is in good agreement with the sum of the ionic radii of V^{2+} (0.79\AA , $\text{CN}=6$) and Cl^- (1.81\AA) ions. The oxidation state of vanadium is confirmed based on bond valence sums (BVS, $0.349 \times 6 = 2.09(4)$) [26].

The structure of the title compound is isotypic with $\text{K}_2\text{MnNb}_6\text{Cl}_{18}$ [13] and $\text{CsTiNb}_6\text{Cl}_{18}$ [14], and is, to our knowledge, the first example of Nb_6 based octahedral cluster compounds stabilized by vanadium as counter-cation. The anticubeoctahedral site, only half occupied in $\text{CsLuNb}_6\text{Cl}_{18}$ and $\text{CsTiNb}_6\text{Cl}_{18}$, is, in clear contrast, fully occupied in the title compound.

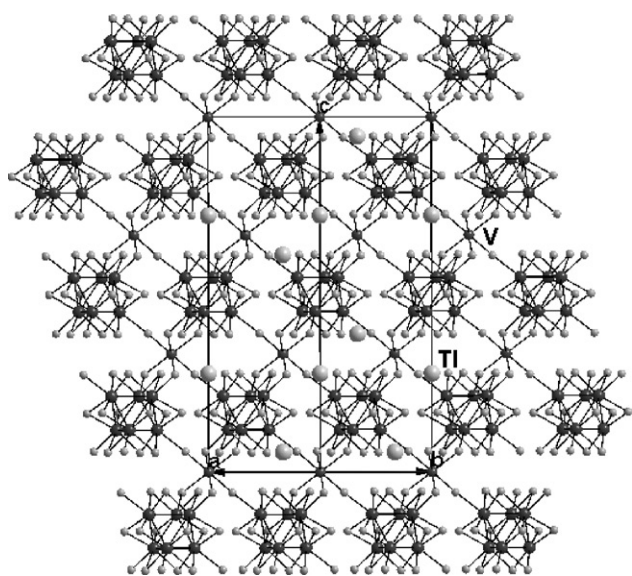


Fig. 2. Projection of the crystal structure of $\text{Tl}_2\text{VNB}_6\text{Cl}_{18}$ in $[110]$ direction shows the layers made by $[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]^{4-}$ units linked via V^{2+} (small black spheres) and Tl^+ (large gray spheres) cations. The layers stack along the c -axis.

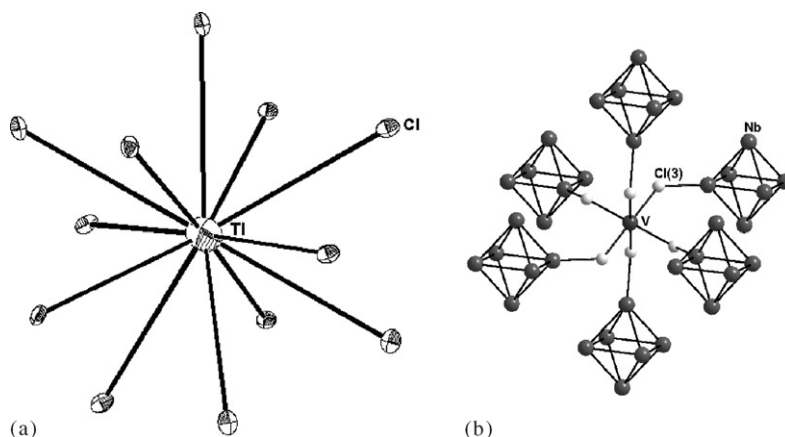


Fig. 3. (a) A view of the anticubeoctahedral coordination geometry of the Tl coordinated to 12 chloride ligands. (b) A view of the octahedral coordination environment of vanadium formed of six outer chloride ligands from six neighboring $[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]$ units.

The inverse molar magnetic susceptibility of the title compound, $\text{Tl}_2\text{VNB}_6\text{Cl}_{18}$ as a function of temperature is shown in Fig. 4. The compound exhibits paramagnetic Curie behavior between 2 and 300 K. The observed effective magnetic moment of $3.37\mu_{\text{B}}$ per formula unit is much lower than the expected value of $3.87\mu_{\text{B}}$ for three unpaired electrons contributed by V^{2+} , and this may be due to the presence of NbOCl_2 in the bulk sample used for magnetic measurement. The electrical resistivity of $\text{Tl}_2\text{VNB}_6\text{Cl}_{18}$ increases exponentially with decreasing temperature (Fig. 5), indicating a semiconducting behavior. The resistivity at room temperature is $9.92 \times 10^2\Omega\text{cm}$. The thermal activation energy for the conduction estimated from the linear fit of the plot of $\ln\rho$ vs $1/T$ in the temperature range 150–300 K is 0.29 eV.

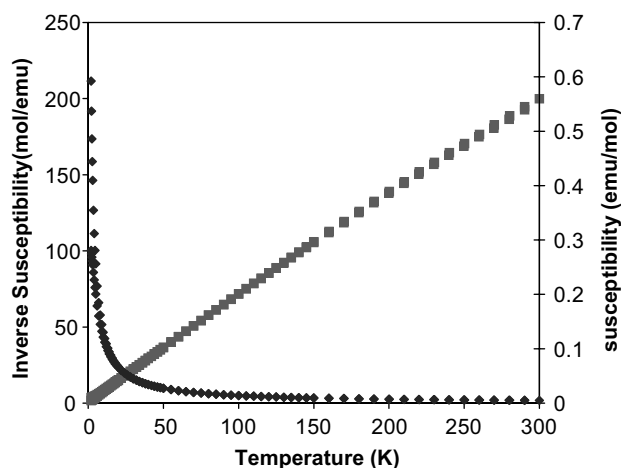


Fig. 4. Magnetic susceptibility curve for $\text{Tl}_2\text{VNB}_6\text{Cl}_{18}$ as a function of temperature: (a) susceptibility vs temperature and (b) inverse susceptibility vs temperature.

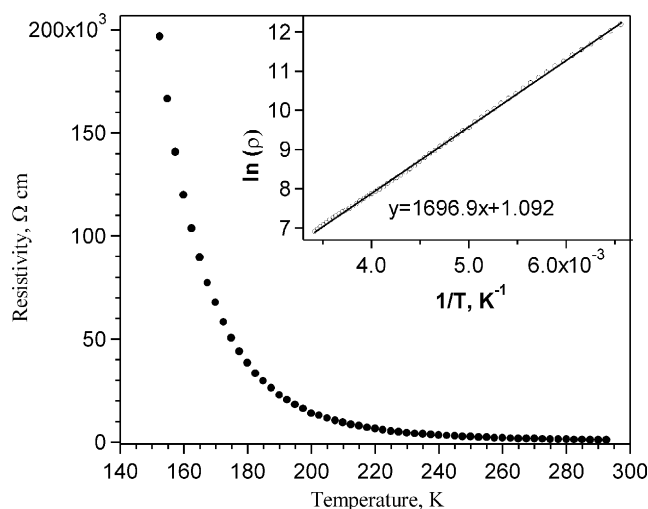


Fig. 5. Electrical resistivity of $\text{Tl}_2\text{VNb}_6\text{Cl}_{18}$ as a function of temperature. (Inset: logarithm of electrical resistivity as a function of $1/T$).

4. Conclusion

A new series of quaternary niobium chloride cluster compounds containing vanadium was prepared for the first time. The crystal structure of $\text{Tl}_2\text{VNb}_6\text{Cl}_{18}$ was determined by single-crystal X-ray diffraction studies. Its structure is isotypic with $\text{K}_2\text{MnNb}_6\text{Cl}_{18}$ or $\text{CsTiNb}_6\text{Cl}_{18}$. The compound contains $[\text{Nb}_6\text{Cl}_{12}\text{Cl}_6]^{4-}$ cluster units with 16 VEC that correlates well with the intra-cluster Nb–Nb bond lengths, indicating that the oxidation state of vanadium is $2+$, as confirmed by V–Cl distances and bond valence sum calculations. The compound exhibits a paramagnetic behavior with an effective magnetic moment of $3.37 \mu_B$.

Acknowledgments

We thank the National Science Foundation, which supports this work through Grant 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 would like to thank Prof. Hans-Conrad zur Loye, University of South Carolina for help with Magnetic Measurements.

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