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STRUCTURE AND CHARACTERIZATION OF THE $[\text{Rb}_x(\text{NH}_4)_{1-x}]_2\text{TeCl}_6$ TELLURATE FAMILY AT ROOM TEMPERATURE

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The crystal structure of rubidium-ammonium hexachlorotellurate $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2\text{TeCl}_6$ was determined by X-ray single crystal analysis at room temperature. The space group is $Fm\bar{3}m$ with the lattice parameter $a = 10.2503(5) \text{ \AA}$ and $Z = 4$. The refinement converged to $R(F) = 0.015$ and $wR(F^2) = 0.032$. As in the studied $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2\text{TeCl}_6$ family, this compound has an antiferite-type arrangement. Tellurium atoms are surrounded by an octahedron of chlorine atoms. The Rb or N atoms are located between TeCl_6^{2-} octahedra ensuring the stabilization of the structure by ionic and hydrogen bonding contacts $\text{N} \cdots \text{H} \cdots \text{Cl}$. The substitution of rubidium by ammonium groups does not affect the structural arrangement, but it leads to a decrease in the a lattice cell dimension. IR and Raman spectroscopic studies at room temperature were performed to confirm the X-ray crystallographic results.

Key words: antiferite type, dynamic motion, substitution, Raman and IR spectroscopy.

INTRODUCTION

In 1957, Gillespie and Nyholm [1] developed valence shell electron-pair repulsion theory, according to which the lone pair of electrons presented in, for example, the hexachlorotellurate (IV) complex anion should be stereochemically active and distort the coordination polyhedron from being regular octahedral. However, several crystal structures of $\text{A}_2[\text{TeX}_6]$ salts (A being an alkali metal and X a halogen) have been determined by X-ray diffraction [2–5], and in all cases reported so far, the coordination was found to be regular octahedral at room temperature. For hexachlorotellurate series of compounds, there is further evidence for the absence of any Gillespie effect: (i) the crystallographic equivalence of the six chlorine atoms of $(\text{NH}_4)_2[\text{TeCl}_6]$ down to liquid-nitrogen temperature shown by nuclear quadrupole resonance experiments [6]; (ii) the absence of any quadrupole splitting in ^{125}Te Mössbauer spectra [7] of $\text{Rb}_2[\text{TeCl}_6]$, $\text{Cs}_2[\text{TeCl}_6]$ and $(\text{NH}_4)_2[\text{TeCl}_6]$ cooled to 80 K. This famous exception to the electron-pair repulsion rules yields to a very symmetric structure at room temperature, which is the antiferite ($\text{K}_2[\text{PtCl}_6]$ -type) structure with the $Fm\bar{3}m$ (O_h^5) space group, except the K_2TeCl_6 compound [2] that adopts the same structure but at higher temperatures; a fact that has been attributed to a small size of the K^+ ion.

Of particular interest is $(\text{NH}_4)_2[\text{TeCl}_6]$ which exhibits a cubic-to-rhombohedral phase transition at 88 K. In order to examine the cationic substitution effect on symmetry and physical properties, we have extended these investigations to $[\text{Rb}_x(\text{NH}_4)_{1-x}]_2\text{TeCl}_6$.

A description of the crystal structure of $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2\text{TeCl}_6$ at room temperature is reported in this paper, as well as the results of thermal analysis (DSC), and room temperature Raman and IR vibrational spectra.

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Table 1

Summary of crystallographic data

Temperature, K	293(2)	Crystal sizes, mm	0.18×0.26×0.47
Formula	[Rb _{0.94} (NH ₄) _{0.06}] ₂ TeCl ₆	Crystal shape	Octahedral
Formula weight	482.54	Radiation (graphite monochromator)	MoK _α ,
Space group	<i>Fm</i> $\bar{3}$ <i>m</i>		$\lambda = 0.71073 \text{ \AA}$
<i>a</i> , \AA	10.2503(5)	θ range for data collection, deg.	5.63 to 36.3
<i>V</i> , \AA^3	1076.99(9)	Total reflections	5265
<i>Z</i>	4	Reflection with ($F > 4\sigma(F)$)	164
ρ_{calc} , g/cm ³	2.018	<i>R</i> (<i>F</i>), %	1.55
μ , mm ⁻¹	7.6	<i>wR</i> (<i>F</i> ²), %	3.25

EXPERIMENTAL

Synthesis and characterization. Tellurium dioxide (TeO₂) was dissolved in a minimum amount of concentrated hydrochloric acid on heating. Two separate solutions of ammonium chloride and rubidium chloride were prepared. The hot solutions were slowly and simultaneously added to the hot tellurium-containing solution. If a precipitate was formed, the mixture was reheated until dissolution. Few drops of concentrated hydrochloric acid were added to the hot solution if necessary.

Slow cooling gave bright yellow octahedral single crystals of [Rb_{*x*}(NH₄)_{1-*x*}]₂TeCl₆, which were filtered and stored for several days in a desiccator containing a small beaker with potassium hydroxide pellets in addition to silica gel. Since hexachlorotellurate crystals are very sensitive to moisture, they were protected by paraffin oil.

The [Rb_{0.94}(NH₄)_{0.06}]₂TeCl₆ formula was determined by refinement of the crystal structure studied at room temperature. The purity was identified by standard tests: tellurium was determined gravimetrically by reduction (SO₂) to the element; using a Kjeldahl apparatus, ammonia was determined by boiling out after the addition of NaOH, collecting the vapor in an aqueous boric acid solution and titrating against standard acid; rubidium was determined using a flame photometer; chlorine was determined after hydrolysis by titration with silver nitrate using a potentiometric method.

Crystal data for [Rb_{0.94}(NH₄)_{0.06}]₂TeCl₆. Crystal data collection was conducted at room temperature on a diffractometer with APEX-II CCD detector. The data were corrected for Lorentz-polarization effects and absorption. A summary of the experiment and structure refinement is given in Table 1.

The positions of tellurium atoms were determined from a three-dimensional Patterson synthesis. Chlorine, rubidium, nitrogen and hydrogen atoms were located by the three-dimensional Fourier analysis. Structure solution and refinement were carried out using SHELX programs [8, 9]. Non-hydrogen atoms were refined anisotropically. The H atoms were attributed isotropic thermal factors close to those of the atoms to which they are linked. Atomic coordinates at room temperature are given in Table 2; bond lengths and bond angles in Table 3; anisotropic displacement parameters in Table 4.

Thermal and spectroscopic analysis. Infrared absorption spectra of suspensions of crystalline powders in KBr were recorded on a PERKIN-ELMER 1750 spectrophotometer in the 400–4000 cm⁻¹ range.

Table 2

Fractional atomic and equivalent thermal parameters (*T* = 293(2) K)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}	Occupation
Te	0	0	0	0.02226(11)	1
Rb	3/4	1/4	1/4	0.049(2)	0.937(3)
N	3/4	1/4	1/4	0.049(2)	0.063(3)
Cl	0	0	0.24655(7)	0.0455(2)	1
H	0.7979(11)	0.2979(11)	0.2979(11)	0.053	0.063(3)

Table 3

Selected bond lengths (\AA) and angles (deg.)

Bond lengths		Angles		Angles	
Te—Cl	2.5272(7)	Cl—Te—Cl	90	Cl—Rb—Cl	120
Rb—Cl	3.6242(2)	Cl—Te—Cl	180	Cl—Rb—Cl	178.88(2)
N—H	0.851	Cl—Rb—Cl	59.09(2)	Cl—Rb—Cl	90
		Cl—Rb—Cl	60.91(2)		

Table 4

Anisotropic displacement parameters (in $10^{-3} \cdot \text{\AA}^2$)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Te	0.0223(1)	0.0223(1)	0.0223(1)	0	0	0
Rb/N	0.0459(2)	0.0459(2)	0.0459(2)	0	0	0
Cl	0.0561(3)	0.0561(3)	0.0212(3)	0	0	0

Raman spectroscopy of polycrystalline samples was performed employing an RTI Dilor instrument using the 514.5 nm line of a Spectra-Physics argon ion laser.

Thermal techniques were employed to characterize possible phase transitions in the title compound. Differential scanning calorimetry (DSC) measurements were carried out using a Setaram DSC121 calorimeter in the 273—523 K temperature range at a heating rate of 5 Kmin^{-1} using a polycrystalline sample placed in a flow of nitrogen.

RESULTS

Structure determination. The structure of this family of salts was first deduced by Wyckoff and Posnjak (1921) [10]. The Te atoms lie at the 4(a) sites of the $Fm\bar{3}m$ (O_h^5) space group, surrounded by an octahedron of halogen atoms in the 24(e) positions with coordinates $(0,0,x)$ and $x \simeq 0.24$. The Rb or N atoms occupy the 8(c) $(3/4, 1/4, 1/4)$ sites, as shown in Fig. 1, and the H atoms (by implication) occupy the 32(f) (x, x, x) sites. Diffraction experiments on the isomorphous $(\text{NH}_4)_2\text{SiF}_6$ by Schlemper et al. (1966) [11] provided information on the orientation and thermal motion of the ammonium group, and similar models of ordering have been used in the structural refinement of $[\text{Rb}_{0.8}(\text{NH}_4)_{0.2}]_2\text{TeCl}_6$ [14] and $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2\text{TeCl}_6$ (this study).

In this family of materials, the ammonium tetrahedron may be placed in two similar positions with its axis along [111], but with either the base or the apex towards the origin. The H atoms occupy the 32(f) positions with $x \simeq 0.19$ and $x \simeq 0.31$ respectively.

DISCUSSION

In the room temperature data refinement, the R factors corresponding to solutions with the two possible sites (see previous section) were 2.26 % and 2.56 % respectively. It was hard to confirm one of the arrangements because the R values were so close. The hydrogen atoms were later placed in each of the 32(f) positions selected from three-dimensional Fourier function and this gave $x_{\text{H}} = 0.7979$, $y_{\text{H}} = 0.2979$, $z_{\text{H}} = 0.2979$ and $R = 1.55$ % leading to an ordered model, and the other parameters are shown in Table 2.

As expected, the salt crystallizes in the $\text{K}_2[\text{PtCl}_6]$ -type cubic face-centered antifluorite structure belonging to the $Fm\bar{3}m$ space group having one formula in the unit cell. The structure is illustrated in Fig. 1. Isolated TeCl_6 octahedra are found to be regular despite the coexistence of two different types of chlorine (the second is H-bonded to ammonium cation when the latter replaces the rubidium cation) with the x_{Cl} value of 0.24655(7), which can be also calculated from the following equation [12]:

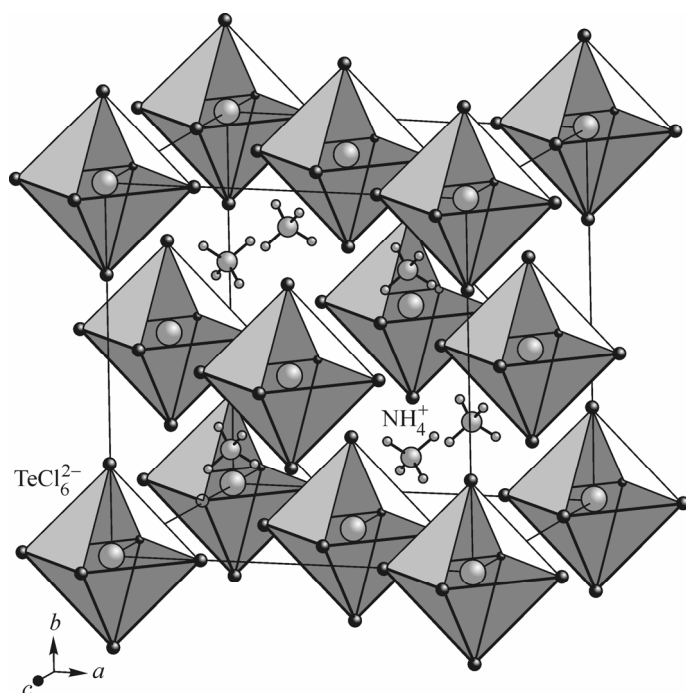


Fig. 1. Room temperature cubic unit cell of $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2\text{TeCl}_6$ having the K_2PtCl_6 type structure

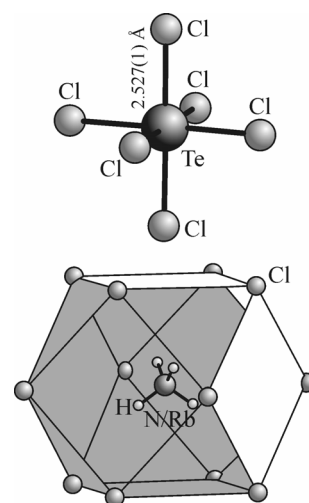


Fig. 2. Te and Rb/N environments in $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2\text{TeCl}_6$

$$x = (0.5 - \sqrt{2} r_{\text{Cl}}/a_0),$$

where x is the chlorine site fractional coordinate.

This correlation between the Te—Cl distance and the unit cell parameter is derived from the fact that Cl^- ions of each octahedron are in contact, as seen in Fig. 1, and this defines a_0 . The calculated value of 0.2462 is in close proximity to that measured indicating that the density of the hexachloride lattice is not affected by the Cl^- — NH_4^+ interaction.

The NH_4^+ tetrahedra, like Rb atoms, reside in the tetrahedral site of the face-centered cubic cell. The presence of both Rb^+ and NH_4^+ cations induces the coexistence of two types of bonds: (1) Ionic bonding between Rb^+ cationic entities and $[\text{TeCl}_6]^{2-}$ anionic complexes. (2) N—H...Cl H-bonding contacts providing a linkage between NH_4^+ cationic entities and $[\text{TeCl}_6]^{2-}$ anionic complexes.

Rb/N atoms are 12-fold coordinated by Cl atom neighbors (Fig. 2). The average distance Rb—Cl is $3.6242(2) \text{ \AA}$.

Comparison of structures in the $[\text{Rb}_x(\text{NH}_4)_{1-x}]_2\text{TeCl}_6$ family. Comparing Rb_2TeCl_6 , $[\text{Rb}_{0.8}(\text{NH}_4)_{0.2}]_2\text{TeCl}_6$ and $(\text{NH}_4)_2\text{TeCl}_6$ compounds we can deduce that the title compound has the same structure but with larger cavity around Rb/N atoms. This increase is caused by the coexistence of the two types of bonds. The values of Te—Cl distances are closer to those observed in Rb_2TeCl_6 rather than to those in $(\text{NH}_4)_2\text{TeCl}_6$.

In order to determine the role of NH_4^+ ions on the stability of the structure, we have studied the evolution of the equivalent thermal parameters of Rb/N versus the NH_4^+ fraction. One can note a relative increase in these values from 0.48 to 0.49, then to 0.51, and then to 0.80 \AA^2 as the ammonium percentage increases from 0 to 6, then to 20, and then to 100 %; this increase indicates the large dynamic motion of NH_4^+ .

Substitution effect on the lattice parameters. With decreasing percentage of ammonium substitution in Rb_2TeCl_6 (Figs. 3 and 4), we can note an increase in the unit cell volume as well as in the a

parameter. This behavior is clearly due to a large difference between the ammonium and rubidium sizes. However, the a and V parameters deviate at $x = 1$, which may suggest a need for reinvestigation of the Rb_2TeCl_6 crystal structure.

SPECTROSCOPIC STUDIES

IR and Raman spectroscopy studies at room temperature were used to analyze a range of observed bands for the mixed compound $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2\text{TeCl}_6$ (Figs. 5 and 6). To assign the Raman and IR peaks to vibrational modes, we examined the modes and frequencies observed for $(\text{NH}_4)_2\text{TeCl}_6$, $[\text{Rb}_{0.8}(\text{NH}_4)_{0.2}]_2\text{TeCl}_6$ [14], and Rb_2TeCl_6 [13].

In the IR spectrum, the presence of the NH_4^+ group can be confirmed by large absorption centered at 3198 cm^{-1} and a band at 3080 cm^{-1} resulting from NH_4^+ antisymmetric stretching vibration, and two other absorption bands at 1708 and 1400 cm^{-1} resulting from NH_4^+ bending vibration.

For the Raman spectrum, the room temperature measured data and reported data [13] for pure compounds are given in Table 5. A comparison between the spectrum of the title compound and other spectra show the usual sharpening and small shifts in band positions for ν_1 , ν_2 , and ν_3 modes relative to TeCl_6^{2-} octahedral vibration. The interesting feature of the new compound is the coexistence of a band at 43 and a shoulder at 90 cm^{-1} identified as ν_{L2} Raman active lattice mode relative to Rb^+ and NH_4^+ translation respectively.

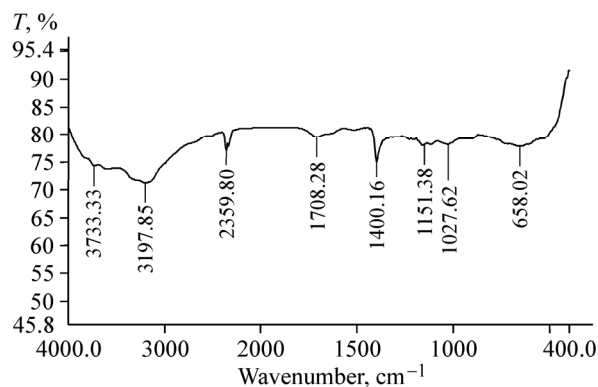


Fig. 5. Raman spectrum of powdered $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2\text{TeCl}_6$ in a glass ampoule at room temperature

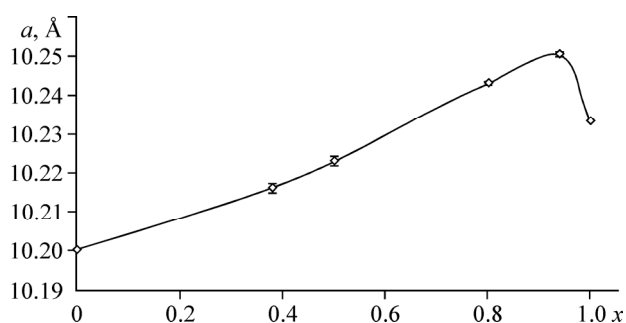


Fig. 3. Ammonium substitution dependence of the a lattice parameter in $[\text{Rb}_x(\text{NH}_4)_{1-x}]_2\text{TeCl}_6$

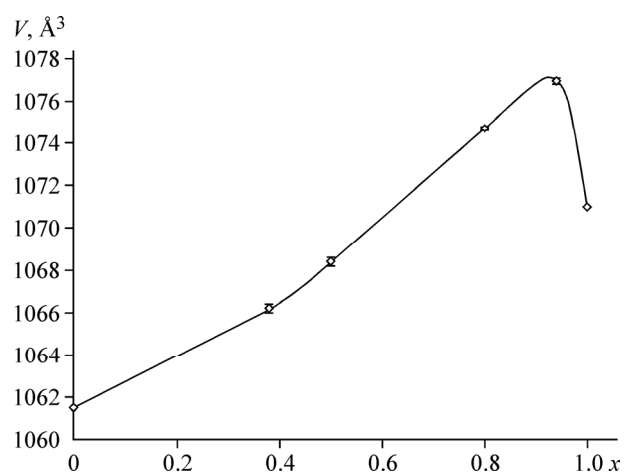


Fig. 4. Ammonium substitution dependence of the unit cell volume in $[\text{Rb}_x(\text{NH}_4)_{1-x}]_2\text{TeCl}_6$

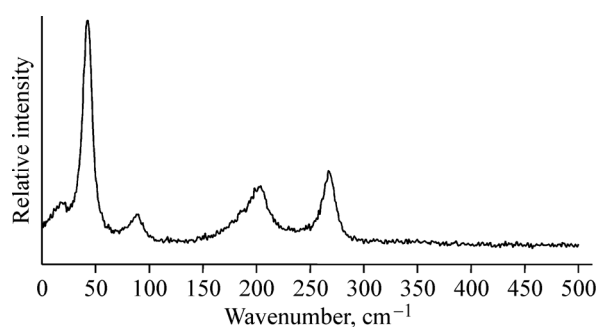


Fig. 6. IR spectrum of $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2\text{TeCl}_6$ at room temperature

T a b l e 5

DSC MEASUREMENTS

Assignment and frequencies (cm^{-1}) observed for Raman spectrum of $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2\text{TeCl}_6$ at room temperature

ν_1 (TeCl str.)	268 s
ν_2 (TeCl str.)	204 m
ν_3 (TeCl bend.)	150 vs
ν_{L2} cation trans.	43/90 vw

Intensity codes: vs — very strong, m — medium, vw — very weak, s — strong.

tetrahedral TeCl_6^{2-} anions. The replacement of rubidium with ammonium cations leads to a decrease in the unit cell volume and the a lattice parameter.

The evolution of the equivalent thermal parameters of N/Rb versus the NH_4^+ fraction shows that this doping leads to an increase in the dynamic motion of the ammonium groups.

No phase transition was found by DSC experiments in the studied temperature range of 273 to 523 K.

The DSC (differential scanning calorimetry) measurements were used to identify the phase transformation temperatures. From the DSC curve of $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2 \times \text{TeCl}_6$ crystals we did not observe any peaks in the studied temperature range of 273—523 K.

CONCLUSIONS

The present paper establishes the crystal structure of $[\text{Rb}_{0.94}(\text{NH}_4)_{0.06}]_2\text{TeCl}_6$ as cubic $Fm\bar{3}m$ at room temperature.

The main feature of the structure of this compound is an antifluorite-type arrangement of $\text{NH}_4^+/\text{Rb}^+$ and

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