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ORIGINAL ARTICLE

Crystal structure at (T = 295 and 173 K) of $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$

R. Karray [a,*], A. van der Lee [b], S. Jarraya [c], A. Ben Salah [a], A. Kabadou [a]

[a] *Laboratoire des Sciences des Matériaux et d'Environnement, Faculté des Sciences de Sfax, BP 1171 3000, Tunisia*
[b] *Institut Européen des Membranes (UMR 5635), Université de Montpellier II, cc 047, Place E. Montpellier, France*
[c] *Ecole préparatoire de l'académie militaire, 3018 Sfax, Tunisia*

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Abstract The crystal structure of lithium–ammonium hexabromotellurate $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$, has been determined by X-ray single crystal analysis at room temperature. The space group is Fm $\bar{3}$ m, with a = 10.7200(12) Å. Differential scanning calorimetry reveals three anomalies at 195, 395 and 498 K. Below 195 K the phase transition leads to a tetragonally distorted structure. This low temperature phase shows an anti-ferrorotative displacement of $TeBr_6^{2-}$ octahedra with a tilt angle 6 °. The title compound has an anti-fluorite-type arrangement of NH_4^+/Li^+ and octahedral $TeBr_6^{2-}$ anions.

1. Introduction

Gillespie and Nyholm (1957), Gillespie (1970) developed the valence shell electron-pair repulsion theory, according to which the lone pair of electrons present in, for example, the hexachlorotellurate(IV) complex anion should be stereochemically active and distort the coordination polyhedron from being regular octahedral (Gillespie effect). However, several X-ray crystal structures of $A_2[TeX_6]$ salts (A being an alkali metal and X an halogen) have been determined (Engel, 1935; Hazell, 1966; Aynsley and Hazell, 1963; Brown, 1964; Webster and Collins, 1973), and in all cases reported so far the coordination was found to be regular octahedral at room temperature.

For compounds A_2TeBr_6 (with A = K, NH_4, Rb, Cs) the high temperature phases show the anti-fluorite ($K_2[PtCl_6]$-type) structure with space group Fm $\bar{3}$ m(Oh^5). On lowering temperature, a second order phase transition can be observed, especially when the anions are comparatively large (Das et al., 1966).

Of particular interest is $(NH_4)_2TeBr_6$, which exhibits a Cubic–Tetragonal phase transition at low temperature. In order to examine the effect and the influence of cationic substitution over symmetry and physical properties, we have extended these investigations to $[(NH_4)_xLi_{1-x}]_2TeBr_6$.

A description of the crystal structure at room and low temperatures of $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$ is reported in this paper.

* Corresponding author. Tel.: +216 74 22200147; fax: +216 74 274 437.
E-mail address: rimrebai@lycos.com (R. Karray).

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2. Experimental

The mixed compound of the composition $[(NH_4)_xLi_{1-x}]_2TeBr_6$ was synthesized by adding the hot saturated solutions of LiBr and NH_4Br and TeO_2 in HBr (1:1:1 mole ratio). The precipitated powder was thoroughly dried and sealed under vacuum. All starting components were of a purity of 99.99 wt.%.

Slow cooling gave bright red octahedral single crystals of $[(NH_4)_xLi_{1-x}]_2TeBr_6$ which were filtered and stored for several days in a desiccators containing a small breaker of potassium hydroxide pellets in addition to the silica gel. As the crystals of the hexabromotellurate are very sensitive to moisture, they were protected by paraffin-oil.

Table 1 Crystal structure data and experimental conditions of structure determination of $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$ at room and low temperatures.

Summary of crystallographic data	T = 295(2) K	T = 173(2) K
Formula	$[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$	$[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$
Space group	Fm $\bar{3}$ m	P4/mnc
a (Å)	10.7200(12)	7.5170(10)
b (Å)	10.7200(12)	7.5170(10)
c (Å)	10.720(2)	10.7153(11)
V (Å^3)	1231.9(3)	605.47(13)
Z	4	2
ρ_{calc} (g/cm^3)	3.542	3.484
μ (mm^{-1})	21.82	22.2
Crystal size (mm^3)	0.25 × 0.3 × 0.4	
F(0 0 0)	1148	
Data collection instrument	OXFORD KM4CCD	
Radiation graphite monochromator λ (Å)	Mo Kα(0.71069)	
Total reflections	348	568
Reflection with ($F > 4\sigma_{(F)}$)	273	449
$R_{(F)}$[a] (%)	4.64	4.9
WR_2[b] (%)	8.69	8.4

[a] $R = \sum ||F_O| - |F_C| / \sum |F_O|$.

[b] $WR_2 = \left[\frac{\sum [w(|F_O|^2 - |F_C|^2)]^2}{\sum [w(|F_O|^2)]^2}\right]$.

The formula $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$ was determined by refinement of the crystal structure at two different temperatures.

The differential scanning calorimetry measurements were performed between 123 and 523 K with a DCS METTLER TA4000 at heating speed of 10 K mn^{-1}.

Crystal data collection procedure and structure refinement, at room and low temperatures, is given in Table 1. Total reflections were collected with OXFORD KM4CCD diffractometer, corrections were made for Lorentz-polarisation effects and absorption.

The positions of the tellurium atoms were determined from a three dimensional Patterson synthesis. Bromine, nitrogen, lithium and hydrogen atoms were located by three-dimensional Fourier function. Structure solution and refinement were carried out using SHELX programs (Sheldrick, 1986, 1997). The non-hydrogen atoms were refined anisotropically. The H atoms were attributed isotropic thermal factors equal to those of the atoms on which they are linked. The atomic coordinates of the room and low temperatures are given in Table 2 while the anisotropic displacement parameters are presented in Table 3.

3. Results

3.1. Calorimetric study

The DSC curve of the $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$ crystals for heating-up is shown in Fig. 1. We observe three endothermic peaks at 195, 395 and 498 K. The corresponding enthalpy changes are $\Delta H1 = 0.24$ J/g, $\Delta H_2 = 6.24$ J/g and $\Delta H_3 = 22.18$ J/g, respectively. The third peak corresponds to the decomposition of the materials.

3.2. Structural properties

3.2.1. Room temperature (298)

The structure of this family of salts was first deduced by Wyckoff and Posnjak (1921). The Te atoms lie on the 4(a) sites of the Fm $\bar{3}$ m(Oh^5) space group, surrounded by an octahedron of halogen atoms in the 24(e) positions with coordinates

Table 2 Positional equivalent isotropic thermal parameters for the structure of $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$ at room and low temperatures.

	x	y	z	U_{eq}	Occupation
T = 295(2)					
Te	0	0	0	0.01595(2)	1
Li				0.0434(4)	0.37(7)
N				0.0434(4)	0.63(4)
Br	0	0.2495(1)	0	0.0548(5)	1
H	0.300(3)	0.199(3)	0.199(3)	0.0434	1
T = 173(2)					
Te	0.0000	0.0000	0.0000	0.0213(3)	1
Li	0.0000	½		0.035(2)	0.37(7)
N	0.0000	½		0.035(2)	0.63(4)
Br(1)	½	½	0.2502(4)	0.050(2)	0.050(2)
Br(2)	0.2267(5)	0.7307(5)	½	0.045(1)	0.045(1)
H	0	0.597(12)	0.202(10)	0.0501	1

$U_{eq} = \frac{1}{3}\sum_i \sum_j Uij a_i^* a_j^* a_i a_j$.

Table 3 Anisotropic displacement parameters (in 10^{-3} Å^2)

	U11	U22	U33	U23	U13	U12
Room temperature						
Te	0.01595(2)	0.01595(2)	0.01595(2)	0	0	0
Li/N	0.0434(4)	0.0434(4)	0.0434(4)	0	0	0
Br	0.0752(7)	0.0752(7)	0.0140(3)	0	0	
Low temperature 173 K						
Te	0.010(1)	0.010(1)	0.013(1)	0	0	0
Li/N	0.047(2)	0.047(2)	0.011(2)	0.011(2)	0.011(2)	0.005(3)
Br1	0.065(2)	0.065(2)	0.021(1)	0	0	0
Br2	0.039(1)	0.032(1)	0.066(2)	0	0	0.0219(8)

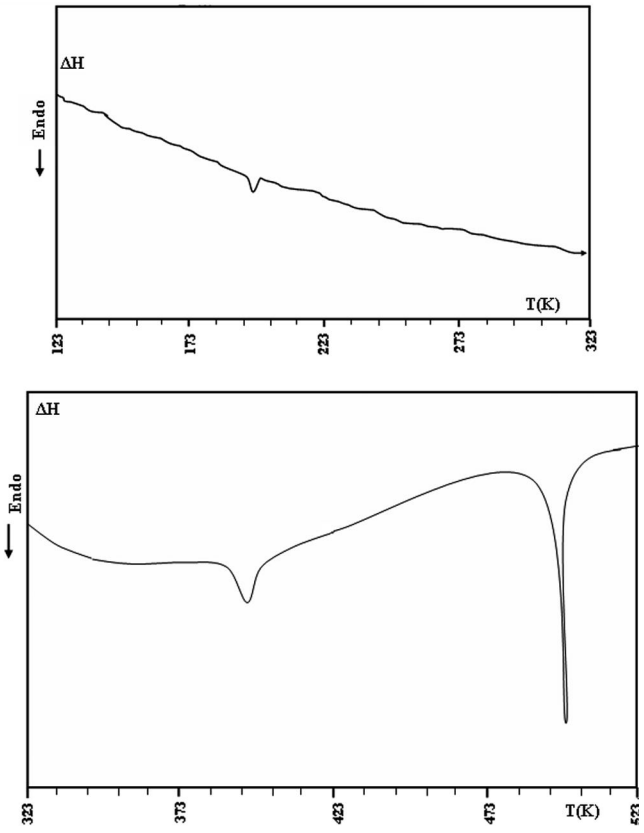

Figure 1 The DSC curves of $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$ for the heating-up runs.

$(x, 0, 0)$ and $x \simeq 0.24$. The average distance Te–Br is 2.6747(4) Å.

The Li or N atoms occupy the 8(c) (, ,) sites, and the H atoms (by implication) the 32(f) (x, x, x) sites. Diffraction experiments on the isomorphous $(NH_4)_2SiF_6$ by Schlemper et al. (1966) have provided information on the orientation and the thermal motion of the ammonium group, and similar models of ordering have been used in this structural refinement of $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$ (see Fig. 2).

The ammonium tetrahedron may be placed in two similar positions with its axis along [1 1 1], 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.

In the room temperature data refinement, the R factors corresponding to the two previous sites are 5.63% and 6.14%,

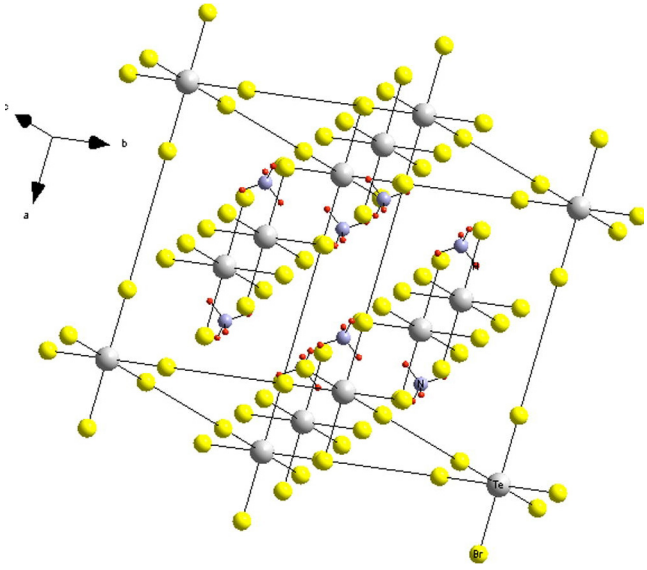

Figure 2 Room temperature cubic unit cell of $[(NH_4)_{0.63}Li_{0.37}]_2$-$TeBr_6$ having the K_2PtCl_6 type structure.

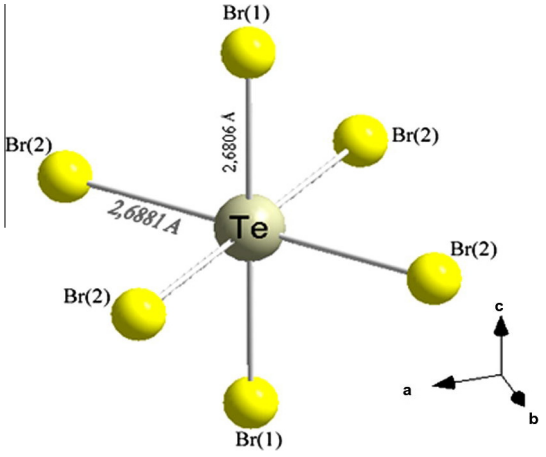

Figure 3 Environment of tellurium atom at 173 K.

respectively. It was hard to confirm one of the tendencies, as the R factors values are very close. The H atom was later placed in the position selected from three-dimensional Fourier function and this gave $x_H = 0.3007$, $y_H = 0.1993$, $z_H = 0.1993$ and $R = 4.64\%$. The H atoms of the ammonium group are orientated with its apex towards the corners, none

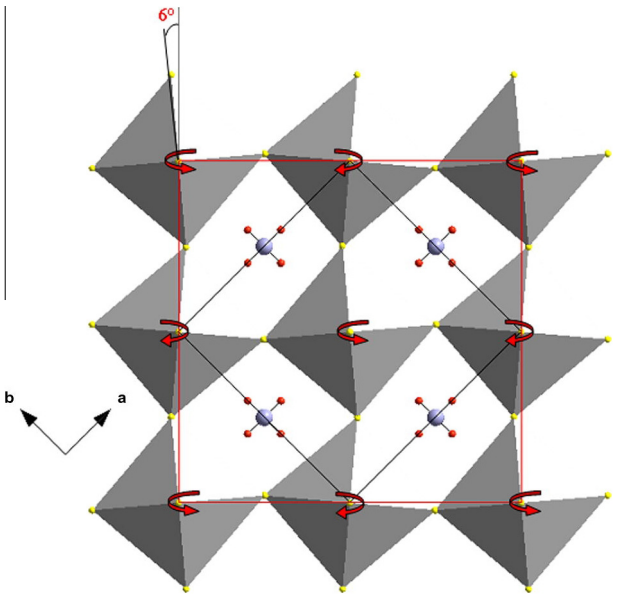

Figure 4 Projection of the tetragonal structure along the 4-fold axis at low temperature.

occupied by Te atoms of the one-eighth cell. The orientation of the ammonium group in $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$ is thus the opposite of that observed at room temperature in $(NH_4)_2SiF_6$.

The NH_4^+ tetrahedra, like Li atoms, reside in the tetrahedral site of the F.C.C cell. This presence of both Li^+ and NH_4^+ cations induce the coexistence of two types of bonds:

- Ionic bonding between cationic entities Li^+ and $[TeBr_6]^{2-}$ anionic complexes.
- H bonding contacts N–H···Br providing a linkage between cationic entities NH_4^+ and $[TeBr_6]^{2-}$ anionic complexes.

Li/N atoms are 12-fold coordinated by Br atom neighbors. The average distance Li–Br is 3.790(2) Å.

3.2.2. Low temperature 173 K

At low-temperature (173 K), $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$ crystallizes in the tetragonal space group (P4/mnc (No. 128)). The tellurium atoms are located on the 4-fold axis along [0 0 1] direction. Each Te atom is surrounded by six Br atoms forming a slightly distorted octahedral structure with the distances 2.6806(2) and 2.6881(3) Å. The small differences of Te–Br bond lengths in the low temperature structure (Fig.3) are not significant considering the standard deviations and are typical for a tetragonal refinement of positional parameters. So the point symmetry of the $TeBr_6^{2-}$ ion is still m3m. There appears to be no stereochemical active lone pair of electrons at Te(IV) in this hexahalogeno complex ion.

The decreasing of the temperature gives the following results:

(a) The thermal motion of Te, Br and Li is reduced. Thus the tellurium atom at low temperature tends to have more ordered and stable octahedral coordination.
(b) An anti-ferrorotative displacement of the $TeBr_6^{2-}$ octahedral (tilt angle 6 °).
(c) The coordination of Li by Br changes from a 12-fold ($Fm\bar{3}m$) to a 4 + 4 + 4 (P4/mnc) one, while the (mean) distances Li–Br decrease from 298 to 175 K.

Fig. 4 shows the tetragonal structure in a projection along the 4-fold axis.

4. Conclusion

The new mixed compound $[(NH_4)_{0.63}Li_{0.37}]_2TeBr_6$ crystallises in the cubic system with the space group $Fm\bar{3}m$ at room temperature (295 K) and in the tetragonal system P4/mnc at 173 K. It appears from this study that no distortion of the type predicted for $[TeBr_6]^{2-}$ by Gillespie and Nyholm has been found at room and low temperatures in the mixed compound. There appears to be no stereochemical active lone pair of electrons at Te(IV) in this hexahalogeno complex ion.

This study shows that the title compound undergoes a phase transition at about 195 K as determined by DSC. This phase transition is characterised by an anti-ferrorotative displacement of the $TeBr_6^{2-}$ octahedral (tilt angle 6 °).

Further experiments should enable us to study the effect of this substitution on phase transition temperatures.

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