Crystal Structure and Phase Transitions of $[C(NH_2)_3]_3Sb_2Cl_9 \cdot 0.9\,H_2O$

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The room temperature structure of $[C(NH_2)_3]_3Sb_2Cl_9 \cdot 0.9\,H_2O$ (GNCA) was solved. It crystallizes in the monoclinic C2/c space group with $a = 15.275$, $b = 8.794$, $c = 17.904$ (in Å), $\beta = 96.40°$, $V = 2390$ Å^3, $Z = 4$. Refinement of the atomic parameters by a least squares methods gave $R = 0.042$, $wR = 0.039$ for 1958 reflections with $F > 4\sigma(F)$. The structure consists of polyanionic $(Sb_2Cl_9^{3-})_n$ layers built of deformed corner connected SbX_6^{3-} octahedra. Two crystallographically inequivalent guanidinium cations are present, one situated between polyanionic layers, the other one together with a disordered water molecule inside cavities formed by polyanions.

Temperature X-ray scattering experiments together with DSC studies were carried out above room temperature. Temperature dependence of the lattice parameters between 300 K and 380 K was determined and a phase transition of mixed order at 364 K was revealed.

Key words: Guanidinium, Chloroantimonate, Crystal structure, Phase transition, DSC.

Introduction

Recently, a number of alkylammonium halogenoantimonates and bismuthates (III) was synthesized. Many of these materials exhibit interesting sequences of phase transitions, some of them to polar piro and ferroelectric phases, see [1] and references cited therein. The mechanisms of the phase transitions are connected with changes in dynamics of cationic sublattices. The high temperature phases are characterized by a considerable freedom of cationic motions. On decreasing the temperature, these motions are consecutively frozen at the phase transitions.

Among several possible stoichiometries in which alkylammonium halogenoantimonates and bismuthates crystallize, most interesting from the point of view of physical properties seems to be the subfamily $R_3M_2X_9$ (R-alkylammonium cation, M-antimony or bismth, X-chlorine, bromine or iodine) [1]. Depending on the size of the alkylammonium cations and the type of halogen atoms there exist three anionic sublattices in which $R_3M_2X_9$ compounds crystallize.

The anions may be built either of polymeric one dimensional chains [2], two-dimensional layers [3] or isolated bioctahedral units [4].

The compounds with small cations crystallize with polymeric anionic sublattices. The alkylammonium cations are located in cavities formed by polyanions. Large cations, which do not fit into polyanionic cavities, crystallize with anionic sublattices built of isolated bioctahedral units composed of two face-sharing MX_6^{3-} octahedra. In such compounds no interesting polar properties have been discovered so far.

$[NH_2(CH_3)_2]_3Sb_2Cl_9$ (DMACA) [5], $[NH_2(CH_3)_2]_3Sb_2Br_9$ (DMABA) [6] and $[NH(CH_3)_3]_3Sb_2Cl_9$ (TMACA) [7], three most interesting polar compounds from the $R_3M_2X_9$ subfamily of halogenoantimonates (III), possess polyanions in the form of two-dimensional layers.

In a search of new compounds with interesting phase transitions and polar properties we tried to substitute the alkylammonium cations by species of comparable size to di- and trimethylammonium cations, to favour the formation of polyanionic sublattices.

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Recently a new compound of $R_3M_2X_9$ stoichiometry, where alkylammonium cations were substituted by guanidinium ones ($C(NH_2)_3^+ = Gu$) $Gu_3Sb_2Cl_9 \cdot 0.9\,H_2O$ (guanidinium nonachloroantimonate = GNCA), was synthesised. The investigations of phase transitions below room temperature were carried out by dielectric, dilatometric DSC and IR spectroscopic methods [8]. A dielectric dispersion below 150 K was found with the activation energy 18 kJ/mole, related to the freezing of the reorientations of guanidinium cations. The character of the changes of the static electric permittivity suggests the presence of a phase transition at 105 K. Morphological studies on GNCA crystals revealed a perfect cleavage plane suggesting a structure analogous to that of DMACA.

In the present work we report on the crystal structure of GNCA at room temperature and on phase transitions in this crystal above room temperature found by the DSC method and by the temperature dependence of lattice parameters.

Experimental

The GNCA crystals were obtained in a reaction of stoichiometric amounts of Sb_2O_3 and guanidinium hydrochloride in hot concentrated hydrochloric acid. They were recrystalized from hydrochloric acid at room temperature. Transparent, prism-shaped crystals were grown by slow evaporation at 295 K. They are plastic with a perfect cleavage plane perpendicular to the c axis.

Data for the structure determination were collected on a KM-4 KUMA diffractometer with Mo K_α radiation ($\lambda = 0.71073$ Å, graphite monochromator). Lattice parameters were refined from setting angles of 23 reflections in the range $17° < 2\theta < 32°$.

A total of 5887 reflections with $5° < 2\theta < 60°$ was collected using the $\omega - \theta$ scan technique (scan speed $0.02-0.08° \, s^{-1}$); scan width 1.4°. After merging ($R_{int} = 0.046$) of 3510 independent reflections, 1958 with $|F_0| > 4\sigma(|F_0|)$ were used for the structure determination. Two control reflections, measured after an interval of 50 reflections show that the intensity variation was negligible. Lorentz, polarization and absorption corrections ($\mu_{Mo\,K_\alpha} = 33.1\,cm^{-1}$) were applied.

Scattering factors for neutral atoms and corrections for anomalous dispersion were as in the SHELXTL PC program system [9]. The SHELXTL PC program was used for all the structure calculations and drawings. A list of the calculated and observed structure factors may be obtained from the authors on request.

The thermal expansion studies were carried out on a single crystal of GNCA using a KM 4 diffractometer. The lattice parameters were refined from setting angles of 25 reflections in the $20° < 2\theta < 30°$ range. The temperature was controlled using an Oxford cryosystem attachment.

Results and Discussion

1. Crystal Structure of GNCA

From the systematic absences the Cc or C 2/c space group follows. Refinement in the noncentrosymmetric Cc space group was unsuccessful, leading to severe correlations, so the C 2/c group was chosen. The structure was solved by the Patterson method and subsequent difference Fourier synthesis which revealed the positions of all non-hydrogen atoms. The hydrogen atoms were added from geometric considerations. The final R and wR were 0.042 and 0.039, respectively, and the goodness of the fit was 1.47.

Before the solution of the crystal structure we anticipated that the structure of $Gu_3Sb_2Cl_9$ is similar to that of $[NH_2(CH_3)_2]_3Sb_2Cl_9$ (DMACA) [8]. After the location of all non-hydrogen atoms from the difference Fourier synthesis there were, however, left two electron peaks of $4\,e/Å^3$ and $3.5\,e/Å^3$. They might be explained by the presence of two crystallographically different disordered water molecules with the occupancy factors 0.25 and 0.2.

To confirm the presence of oxygen atoms in the crystal structure we carried out an experiment on the Energy Dispersive Analysis of X-rays on a microanalyzer EDAX EDX 9800. From the analysis follows the molar ratios (N + C : O : Cl : Sb = 11.7 : 0.7 : 9.4 : 2. The theoretical ratios for $Gu_3Sb_2Cl_9 \cdot 0.9\,H_2O$ are N + C : O : Cl : Sb = 12 : 0.9 : 9 : 2. This analysis confirmed unequivocally the presence of oxygen in the crystal structure.

The calculated density for the hydrate is 2.104 g/cm^3. The density measured by flotation gave 2.04(1) g/cm^3. The smaller than calculated density may be explained by the structure of the polyanionic two-dimensional layers which are not connected with each other by hydrogen bonds. By the presence of small defects (dislocations) the crystal is able to possess large

empty voids between the layers which would lead to a smaller than calculated density.

The C, N and H weight concentrations for $Gu_3Sb_2Cl_9$ are 4.85, 2.42 and 16.97, whereas for $Gu_3Sb_2Cl_9 \cdot 0.9\,H_2O$ they are 4.70, 2.60 and 16.61. From elemental analysis of the twice recrystallized crystal they were 4.70, 2.50 and 16.60. The differences of the C, N and H concentrations among these two salts are small, but the experimental results seem to confirm the assumed formula.

Table 1 shows the crystal data for GNCA crystal together with the measured parameters, Table 2 the atomic co-ordinates and equivalent isotropic displacement coefficients and Table 3 the inter-atomic distances and angles.

The anionic sublattice of GNCA crystal is built of polymeric two dimensional $(Sb_2Cl_9^{3-})_n$ layers lying in the ab plane. The layers consist of deformed $SbCl_6^{3-}$ octahedra, corner-connected in such a way that three chlorine atoms of the co-ordination sphere of each antimony atom are bridging whereas the other three are terminal.

Table 1. Crystal data of GNCA and the measured parameters.

Empirical formula	$(C(NH_2)_3)_3Sb_2Cl_9 \cdot 0.9\,H_2O$
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	$a = 15.275\,(3)$ Å
	$b = 8.794\,(2)$ Å
	$c = 17.904\,(4)$ Å
	$\beta = 96.40\,(3)°$
Volume	2390.0 (9) Å^3
Z	4
Density (calc.)	2.104 g/cm^3
Density (meas.)	2.04 (1) g/cm^3
Absorption coefficient	3.306 mm^{-1}
Temperature	298 K
Index ranges	$-24 \le h \le 24$, $0 \le k \le 13$
	$-19 \le l \le 19$
Reflections collected	5887
Independent reflections	3510 ($R_{int} = 4.62\%$)
Observed reflections	1958 ($F > 4.0\,\sigma$ (F))
Refinement method	Full-matrix last-squares
Quantity minimized	$\Sigma\, w\,(F_0 - F_c)^2$
Extinction correction	$\chi = 0.00026\,(2)$, where
	$F^* = F\,[1 + 0.002\,\chi\,F^2/\sin(2\theta)]^{-1/4}$
Hydrogen atoms	Riding model, fixed isotropic U
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0000\,F^2$
Number of parameters refined	138
Final R indices (obs. data)	$R = 4.22\%$, $wR = 3.89\%$
Goodness-of-fit	1.47
Largest difference peak	$+1.11$, -0.82 e Å^{-3}

Table 2. Atomic coordinates ($\cdot 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \cdot 10^3$) of GNCA. The equivalent isotropic U is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	X	Y	Z	U_{eq}
Sb(1)	6556 (1)	5989 (1)	1664 (1)	30 (1)
Cl(1)	5801 (1)	3968 (3)	900 (1)	42 (1)
Cl(2)	7784 (1)	5970 (2)	891 (1)	40 (1)
Cl(3)	5804 (1)	7912 (3)	833 (1)	50 (1)
Cl(4)	5000	6040 (4)	2500	46 (1)
Cl(5)	7510 (2)	3505 (2)	2501 (2)	47 (1)
C(1)	5000	1027 (17)	2500	75 (4)
N(1)	5451 (9)	2272 (15)	2692 (10)	60 (5)
N(2)	4199 (8)	1065 (19)	2684 (9)	64 (4)
N(3)	5439 (9)	−237 (15)	2646 (10)	62 (5)
C(2)	8145 (5)	10974 (10)	884 (4)	44 (2)
N(4)	8562 (4)	9662 (7)	835 (4)	51 (3)
N(5)	8557 (5)	12229 (8)	889 (5)	59 (3)
N(6)	7279 (4)	10966 (9)	884 (4)	55 (2)
O(1)	8538 (9)	4047 (20)	1676 (9)	20 (4)
O(2)	4595 (10)	3991 (26)	1642 (14)	25 (5)
H(1A)	5215	3052	2925	80
H(1B)	6010	2333	2578	80
H(2A)	4019	1897	2917	80
H(2B)	3829	275	2586	80
H(3A)	5199	−1005	2886	80
H(3B)	5991	− 322	2520	80
H(4A)	8255	8786	797	80
H(4B)	9151	9648	830	80
H(5A)	9139	12220	850	80
H(5B)	8275	13119	932	80
H(6A)	6990	10073	845	80
H(6B)	6980	11837	926	80

Table 3. Bond lengths (Å) and angles (°) in GNCA.

Sb(1)−Cl(1)	2.450 (2)	Cl(1)−Sb(1)−Cl(2)	91.3 (1)
Sb(1)−Cl(2)	2.453 (2)	Cl(1)−Sb(1)−Cl(3)	90.1 (1)
Sb(1)−Cl(3)	2.451 (2)	Cl(1)−Sb(1)−Cl(4)	86.5 (1)
Sb(1)−Cl(4)	2.946 (2)	Cl(1)−Sb(1)−Cl(5)	85.5 (1)
Sb(1)−Cl(5)	2.942 (2)	Cl(1)−Sb(1)−Cl(5A)	176.6 (1)
Sb(1)−Cl(5A)	2.948 (2)	Cl(2)−Sb(1)−Cl(3)	89.9 (1)
C(1)−N(1)	1.319 (18)	Cl(2)−Sb(1)−Cl(4)	176.2 (1)
C(1)−N(2)	1.302 (12)	Cl(2)−Sb(1)−Cl(5)	85.2 (1)
C(1)−N(3)	1.309 (18)	Cl(2)−Sb(1)−Cl(5A)	86.2 (1)
C(2)−N(4)	1.325 (11)	Cl(3)−Sb(1)−Cl(4)	87.1 (1)
C(2)−N(5)	1.270 (12)	Cl(3)−Sb(1)−Cl(5)	173.3 (1)
C(2)−N(6)	1.323 (10)	Cl(3)−Sb(1)−Cl(5A)	87.6 (1)
		Cl(4)−Sb(1)−Cl(5)	97.7 (1)
		Cl(4)−Sb(1)−Cl(5A)	95.9 (1)
		Cl(5)−Sb(1)−Cl(5A)	96.6 (1)
		Sb(1)−Cl(4)−Sb(1A)	178.3 (1)
		Sb(1)−Cl(5)−Sb(1B)	179.2 (1)
		N(1)−C(1)−N(2)	113.0 (13)
		N(1)−C(1)−N(3)	114.3 (8)
		N(2)−C(1)−N(3)	116.5 (13)
		N(4)−C(2)−N(5)	121.1 (8)
		N(4)−C(2)−N(6)	118.9 (8)
		N(5)−C(2)−N(6)	119.9 (8)

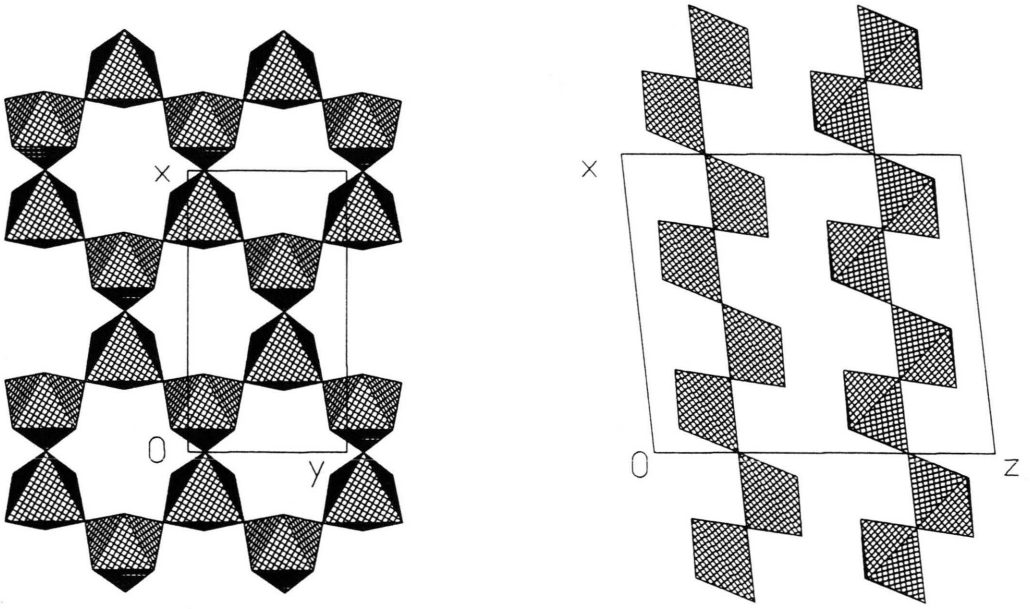

Fig. 1. The projection of the anionic sublattice of GNCA onto the *b* and *c* directions in the polyhedral representation.

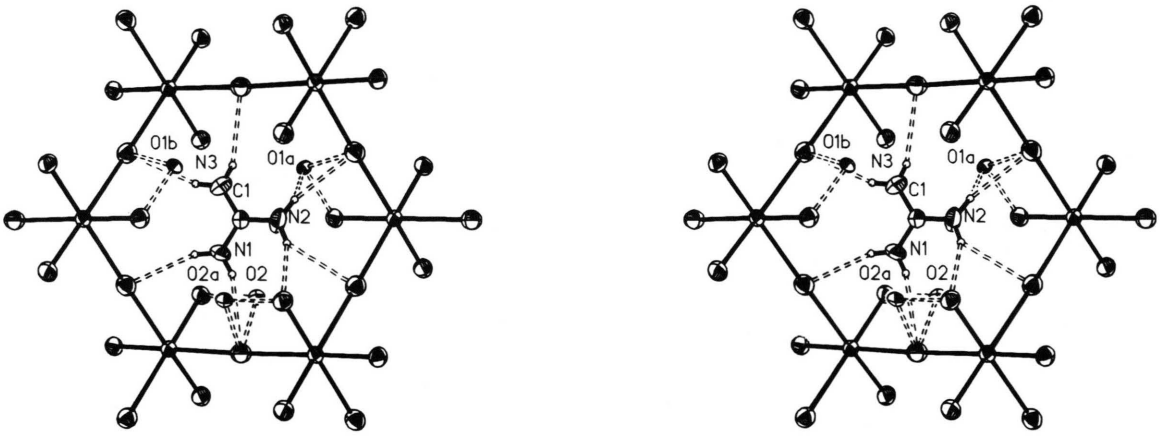

Fig. 2. Stereo picture of the cavity inside the polyanionic sublattice. For clarity, only one position of the disordered guanidinium cation is shown. The dashed lines represent hydrogen bonds which tie the guanidinium cation to the polyanionic sublattice. The positions of the two closest contacts for each oxygen atom are also shown by dashed lines.

Schematic projections of the anionic sublattice onto the b and c directions are presented in Figure 1. There are two types of vacancies in the crystal structure of GNCA. One, situated inside the polyanionic layers, is formed by twelve membered Sb – Cl – Sb rings. This vacancy has the shape of a cube cut perpendicular to the C_3 axis. The other type of vacancy is situated between the polyanionic layers.

Two types of crystallographically inequivalent guanidinium cations occupy the vacancies. One situated between the $(Sb_2Cl_9^{3-})_n$ layers, the other one, together with statistically disordered water molecules, in the cavity formed by six $SbCl_6^{3-}$ octahedra inside the polyanionic layer (The stereo picture of this void is presented in Figure 2). Both guanidinium cations are planar and parallel to each other.

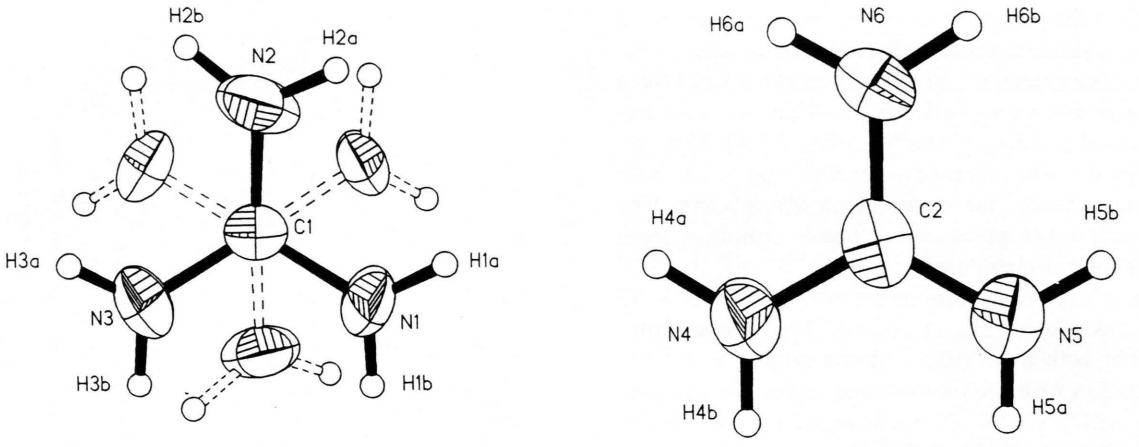

Fig. 3. Picture of two crystallographically inequivalent guanidinium cations showing the atomic numbering.

Table 4. Lengths (Å) and angles (°) of possible hydrogen bonds in GNCA.

	X–H	H...Y	X...Y	angle X–H...Y
N1 H1A Cl4	0.90	2.748 (10)	3.394 (14)	129.2 (15)
N1 H1B Cl5	0.90	2.532 (15)	3.380 (14)	157.3 (16)
N2 H2A Cl1	0.90	2.779 (18)	3.598 (17)	151.4 (17)
N2 H2A Cl5	0.90	2.762 (16)	3.366 (14)	125.3 (16)
N2 H2B Cl5	0.90	2.541 (16)	3.413 (15)	164.6 (18)
N2 H2B O1	0.90	1.973 (24)	2.651 (22)	131.3 (18)
N3 H3A Cl4	0.90	2.695 (18)	3.346 (14)	129.5 (16)
N3 H3B Cl5	0.90	2.518 (16)	3.360 (14)	156.4 (17)
N4 H4A Cl2	0.90	2.590 (9)	3.463 (7)	163.2 (6)
N4 H4B Cl1	0.90	2.581 (3)	3.463 (8)	166.8 (6)
N5 H5A Cl3	0.90	2.617 (3)	3.497 (8)	165.5 (7)
N5 H5B Cl2	0.90	2.617 (9)	3.495 (7)	166.3 (7)
N6 H6A Cl3	0.90	2.622 (7)	3.500 (8)	164.9 (6)
N6 H6B Cl1	0.90	2.594 (7)	3.476 (8)	165.9 (6)

The cation located inside the polyanionic cavity is disordered. The disorder is realized by the distribution of the nitrogen atoms between two positions with an occupation factor 0.5. A picture of the cations, showing the atomic numbering, is presented in Figure 3.

In Table 4 the lengths of possible hydrogen bonds in GNCA are presented. The N...Cl shortest contacts fall in the range 3.35–3.60 Å, corresponding to rather weak hydrogen bonds. The lengths of the N...Cl contacts in GNCA are similar to those found in guanidinium chloride [10].

The oxygen atoms are located close to the chlorine atoms. The presence of oxygen atoms arises from the presence of disordered water molecules, however the positions of the hydrogen atoms could not be determined from the difference Fourier synthesis. If the hydrogen atoms are located between O and Cl atoms, the O–H...Cl contacts of 2.32–2.40 Å are very short for hydrogen bonds. To confirm this possibility, we checked these distances in structures of over 2300 hydrates in the Cambridge Structural Database. We found out that such short O...Cl bonds exist [11, 12]. Recently $(H_2O \cdot Cl^-)_3$ planar cyclic hydrogen rings have been found with O...Cl^- distances of 2.46 (4) Å, close to that observed in GNCA [11].

The lengths of the Sb–Cl contacts vary between 2.450 and 2.948 Å with the three long bonds characteristic for bonding chlorine atoms (2.942, 2.946 and 2.948 Å) and three short ones (2.450, 2.451 and 2.453 Å) for terminal chlorine atoms opposite to the bonding ones. It should be noted that the sums of the bond-lengths between antimony and opposite chlorine atoms are equal to each other (Sb1–Cl1 + Sb1–Cl5′ = Sb1–Cl2 + Sb1–Cl4 = Sb1–Cl3 + Sb1 –Cl5 = 5.399 Å). A similar situation was found in the $Gu_2SbCl_5 \cdot GuCl$ (GHCA) crystal with this sum equal to 5.395 Å [13].

The Cl–Sb–Cl angles are close to 90° (between 85° and 98°). The Sb–Cl bond-lengths and the Cl–Sb–Cl angles are similar to those found in other halogenoantimonates [2–7].

The characteristic feature of alkylammonium halogenoantimonates and bismuthates is the octahedral co-ordination of the antimony (bismuth) atoms. The anions are formed by the MX_6^{3-} octahedra connected with each other by corners, edges or faces forming isolated units or polymeric structures. A short

review of the polymeric structures most characteristic for the alkylammonium halogenoantimonates has recently been presented [13]. In all these structures there are large differences between M–X distances for terminal and bonding contacts (of 0.5–0.7 Å). They are explained by the presence in the Sb^{3+} ion of lone-pair electrons which are stereochemically inactive. The lone pair takes place in the bond forming a three bonds four electron center.

The guanidinium cations are planar. Their C–N3 skeletons possess D_{3h} symmetry. The carbon atoms together with the nitrogen atoms exhibit on sp^2 hybridization with the inter atomic angles close to 120° (113°–121°). The C–N bonds acquire partial double bond character (1.27–1.33 Å) because of delocalization of the lone pair electrons of the nitrogen atoms with a vacant p_z orbital of the carbon atom. These results agree with results of other authors studying compounds containing guanidinium cations [10, 14].

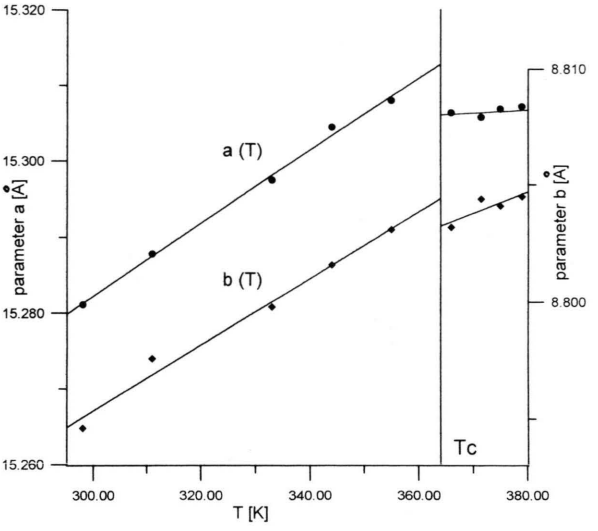

Fig. 4. Temperature dependence of the *a* and *b* lattice parameters of GNCA in the vicinity of phase transition at 364 K.

2. *DSC Studies*

The DSC studies on GNCA were carried out between 300 and 400 K. One small heat anomaly was found at 363 K. The transition enthalpy is 0.6 kJ/mole and the transition entropy 1.7 J/K · mole. The shape of the DSC curve and the values of the observed effects suggest a transition of mixed order.

3. *Temperature Dependencies of Lattice Parameters*

In Figs. 4 and 5 the temperature dependences of the lattice parameters *a*, *b*, *c*, and β for the GNCA crystal between 300 and 380 K are shown.

Between 300 and 364 K and between 364 and 380 K the lattice parameters were fitted by a least squares method. $c(T)$ and $\beta(T)$ show small changes across the phase transition, whereas *a* and *b* decrease significantly at T_c. The temperature dependences of the lattice parameters confirm the presence of the phase transition found by the DSC method. The mechanism of this transition is not clear.

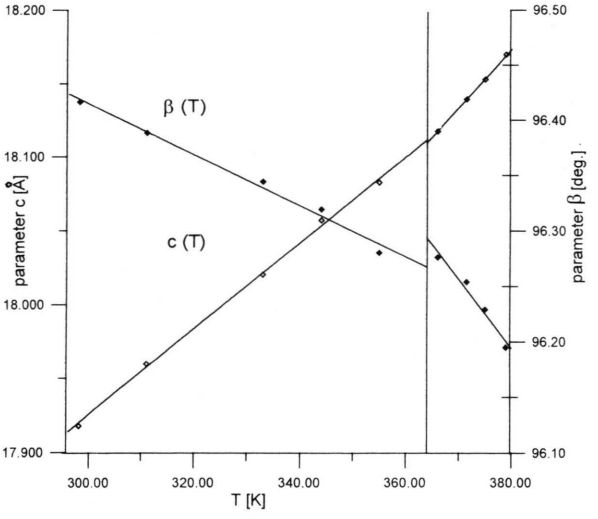

Fig. 5. Temperature dependences of the lattice parameter *c* and the angle β of GNCA in the vicinity of phase transition at 364 K.

The dielectric studies on GNCA below room temperature did show a relaxation process in the kHz frequency-range below 150 K. The character of the static electric permittivity changes suggested the presence of a phase transition at 105 K. On decreasing the temperature, the motions of the dipoles become too slow to reorient with the frequency of the applied electric field. Since GNCA possesses a polyanionic sublattice, the dielectric dispersion must be due to the freezing of reorientations of the cations [8].

The characteristic feature of many solid guanidinium salts is the presence of reorientational motions of the cations. The NMR studies show that the guanidinium cations undergo reorientations around the C_3 axis [15].

The height of the potential barrier estimated from the dielectric studies (18 kJ) on GNCA is similar to the energy barriers for the C_3 type of reorientations of the guanidinium cations obtained from NMR studies. The dielectric dispersion, observed in GNCA, results from the freezing of the reorientations of at least one of the crystallographically inequivalent guanidinium cations [8]. It seems probable that this process is due to a hindered rotation of the cation situated in the polyanionic cavity, stabilized after each jump by hydrogen bonds. Such reorientations may freeze on decreasing the temperature, leading to the microwave dispersion observed in the dielectric studies.

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[1] R. Jakubas and L. Sobczyk, Phase Transitions **20,** 163 (1990).
[2] K. Kihara and T. Sudo, Acta Cryst. **B 30,** 1088 (1974).
[3] K. Kihara and T. Sudo, Z. Kristalogr. **134,** 142 (1971).
[4] M. Hall, M. Nunn, M. J. Begley, and D. B. Sowerby, J. Chem. Soc. Dalton Trans. 1231 (1986).
[5] M. Gdaniec, Z. Kosturkiewicz, R. Jakubas, and L. Sobczyk, Ferroelectrics **77,** 31 (1988).
[6] R. Jakubas, L. Sobczyk, and J. Matuszewski, Ferroelectricts **74,** 339 (1987).
[7] A. Kallel and J. W. Bats, Acta Cryst. **C 41,** 1022 (1985).
[8] J. Zaleski, R. Jakubas, G. Bator, and J. Baran, J. Mol. Struct. **325,** 95 (1994).
[9] SHELXTL PC Program System Siemens Analytical X-ray Instruments Inc., Madison WI 1990.
[10] J. M. Adams and R. W. H. Small, Acta Cryst. **B 32,** 832 (1976).
[11] L. Book and T. C. W. Mak, Inorg. Chim. Acta **92,** 265 (1984).
[12] M. R. Bond and R. D. Willet, Acta Cryst. **C 43,** 2304 (1987).
[13] J. Zaleski and A. Pietraszko, J. Mol. Structure (in press).
[14] D. J. Haas, D. R. Harris, and H. H. Mills, Acta Cryst. **19,** 676 (1965).
[15] S. Gima, Y. Furukawa, and D. Nakamura, Ber. Bunsenges. Phys. Chem. **88,** 939 (1984).