CRYSTALLOGRAPHIC PARAMETERS OF 1-ORGANYLGERMATRANES

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The crystallographic parameters and the translation groups of the elementary cells of the crystals of 1-methyl-, 1-ethyl-, 1-phenyl-, and 1-α-naphthylgermatranes have been determined by X-radiography. The volumes of the elementary cells (V), the number of molecules in them (N), the X-ray density of the crystals (σ_X) and the packing coefficients for the molecules in the crystals (k) have been calculated from the linear and angular parameters.

In a preceding paper [1], one of us began the determination of the crystallographic parameters of the metalloatranes [2] and, in particular, determined the constants of the elementary cells of the crystals of a number of silatranes. This work is a continuation of the X-ray-structural study of this series of compounds and is devoted to a determination of the parameters of the elementary cells of the crystals of the 1-organylgermatranes [2, 3].

Since Si and Ge are chemical elements having similar configurations of the outer electron shell and also very similar atomic radii [4] (r_{Si} = 1.17Å, r_{Ge} = 1.22Å), it was natural to expect that the crystal structures of the corresponding silatranes and germatranes would be similar. This question can be answered by determining the symmetry and parameters of the elementary cells, and also by a qualitative comparison of the developments of the layer lines of the reciprocal lattices of crystals of corresponding silatranes and germatranes. The finding of the existence of isomorphism in the crystals of corresponding compounds of these two series was also important in the selection of the most suitable compounds for the study of the complete crystal structure of the atranes since the germatranes, containing the heavier Ge atom, are more suitable for this purpose than the silatranes.

The single crystals of the 1-organylgermatranes that were studied, like the corresponding silatranes, form more or less elongated colorless needles possessing only one face zone, the axis of which coincides with the axis of the needle itself. The imperfection of the external faceting of the crystals of the germatranes considerably complicated the centering and aligning of the crystals.

The mounting of the single crystals in the cameras was carried out with the aid of an optical illuminator. A check of the positioning and also the matching of definite crystallographic directions of the elementary cells with the axis of oscillation or rotation was done from the Laue patterns.

To obtain the experimental material we used the oscillating and rotating methods with the development of the layer lines in reciprocal lattice cameras (KFOR). The time of exposure in the preparation of the oscillating X-ray diagrams in the range of angles up to 20° was 8–10 hr. The time of exposure in the preparation of the Kforograms* varied from 80 to 120 hr, according to the particular layer line. The investigation was carried out with copper radiation, λ_{Cu} = 1.54Å. The crystals of the germatranes, like those of the silatranes, are very stable to X-radiation.

The crystallographic characteristics of 1-methyl-, 1-ethyl-, 1-phenyl-, and 1-α-naphthylgermatranes are given in the table.

On comparing the parameters of the elementary cells of the methyl-, ethyl-, phenylsilatranes [1] and the corresponding germatranes, it can be seen that both 1-methylsilatrane and 1-methylgermatrane crystallize in the monoclinic system with a monoclinic angle β = 122.6° for methylsilatrane and 122° for methylgermatrane. The crystals of the other germatranes studied are rhombic. As a rule, the linear parameters of the elementary cells of the germatranes are greater than the corresponding parameters of the elementary cells of the silatranes. This is a consequence of the difference in the radii of the germanium and silicon atoms with an ordinary covalent bond. However, in no case does the difference in the parameters exceed 0.3Å. This fact, particularly if one bears in mind the error in

*From "KFOR"

determination of the parameters of the elementary cells by the oscillating method, allows one to conclude that the corresponding compounds of the silatrane and germatrane series crystallize isostructurally.

Crystallographic Parameters of Some 1-Organogermatranes

$R—Ge(OCH_2CH_2)_3N$

R	a, Å	b, Å	c, Å	β	V, Å^3	N	$\frac{V}{N}$, Å^3	σ_p, g/cm^3	σ_x, g/cm^3	R, Å^3	k, %
CH_3—	7,60	9,69	14,38	122°	898,02	4	224,51	1,70	1,71	24,93	72,4
CH_3CH_2—	9,34	16,75	6,72		1051,31	4	262,83	1,591	1,561	41,49	68,8
C_6H_5—	13,19	18,63	10,09		2479,42	8	309,93	1,62	1,58	78,99	70,5
α-$C_{10}H_7$—	9,57	14,54	10,64		1480,53	4	370,13	1,61	1,596	122,39	70,8

This is also confirmed by a comparison of the developments of the layer lines of the reciprocal lattices of the crystals of corresponding compounds.

In order to determine the translation group, oscillating X-radiograms along the faces and three-dimensional diagonals of the elementary cells of the crystals of the 1-organylgermatranes were taken. A comparison of the experimental and calculated identity periods along these directions show that the elementary cells of all the germatranes studied are primitive.

On the basis of the parameters obtained for the elementary cells, the interatomic distances, and the covalent radii of the atoms present in the germatrane molecules, and the intermolecular radii of the corresponding atoms known from the literature [5], we calculated the packing coefficients of the molecules in the germatrane crystals (k).

The summation of the increments calculated by the method discussed in the previous paper [1] gave the volume of the germatrane part of the molecule as 139.86 Å [3] where the germanium atom was attached to an aliphatic carbon atom, and 139.54 Å [3] for an aromatic carbon atom. The volumes of the substituents R and the values of the packing coefficients k are given in the table.

The most suitable compounds for the complete determination of molecular and crystal structure are 1-ethylgermatrane and 1-α-naphthylgermatrane.

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