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Cluster Self-Organization of Intermetallic Systems: New Two-Layer Cluster-Precursor K46 = 0 @8(Ca$_2$Hg$_6$)@38(Hg$_6$ + CaHg$_6$)$_2$(Ca$_6$Hg$_6$) for Self-Assembly of the Crystal Structure of Ca$_{11}$Hg$_{54}$–*hP*65

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Abstract—A combinatory topological analysis and simulation of the self-assembly of the crystal structure of Ca$_{11}$Hg$_{54}$–*hP*65 ($a = b = 17.114$ Å, $c = 10.442$ Å, hexagonal group *P*-6) are performed by computer methods (ToposPro software package). A total of 184 variants of the cluster representation of the 3D atomic lattice with a number of structural units of 3–7 are established. The polyhedral clusters K8 = 0@Ca$_2$Hg$_6$, which appeared to be hexagonal bipyramids, the polyhedral clusters K11 = 0@Ca$_3$Hg$_8$, and the polyhedral clusters with the central Hg atom K12 = Hg(Ca$_3$Hg$_8$) are determined. The centers of the Ca$_2$Hg$_6$, 0@Ca$_3$Hg$_8$ and Hg(Ca$_3$Hg8) clusters occupied the highly symmetric positions 1*c*, 1*b*, and 1*f* with a –6 symmetry. The precursor clusters Ca$_2$Hg$_6$ represent templates on the surface of which atomic shells of 38 atoms are formed. The composition of the two-layered template cluster K46 is 0@8(Ca$_2$Hg$_6$)@38(Hg$_6$ + CaHg$_6$)$_2$(Ca$_6$Hg$_6$). The symmetry and topological code for the self-assembly processes of the 3D structure from the nanoclusters-precursors K46 with participation of the polyhedral clusters 0@Ca$_3$Hg$_8$ and Hg(Ca$_3$Hg$_8$) are simulated.

Keywords: intermetallide Ca$_{11}$Hg$_{54}$–*hP*65, self-assembly of crystal structure, polyhedral clusters K8 = Ca$_2$Hg$_6$ and K12 = Hg(Ca$_3$Hg$_8$), two-layered cluster K46 = 0@8(Ca$_2$Hg$_6$)@38(Hg$_6$ + CaHg$_6$)$_2$(Ca$_6$Hg$_6$)

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INTRODUCTION

The crystal chemistry family of double Hg intermetallides includess about 200 compounds [1]. The formation of Hg intermetallides was established in 45 *A*–Hg systems. The largest number of crystallochemically different intermetallides (eleven) was found in the binary system Ca–Hg, with a wide range of changes in the Hg : *A* atomic ratio from 11 to 0.33 (Table 1, [2–6]).

The crystal structures of six Hg-intermetallides were included in the crystal chemistry families of the most common types of crystal structures, with several hundred specimen each. Three Hg intermetallides belonged to the crystal chemistry families with more than forty species (Table 1). The authors of [7, 8] simulated the cluster self-assembly of widely spread types of crystal structures established for Hg intermetallides.

The most crystallochemically complex family of intermetallides Ca$_{11}$Hg$_{54}$–*hP*65 included two more compounds: Sr$_{11}$Hg$_{54}$–*hP*65 [5] and Yb$_{11}$Hg$_{54}$–*hP* [9]. The crystal structure of the intermetallide Ca$_{11}$Hg$_{54}$–*hP*65 [5] with the spatial group *P*-6 (no. 174) and $V = 1492.7$ Å^3 was characterized by 18 crystallographically independent atoms with the Wyckoff sequence *l*^{6}*k*^{3}*j*^{4}*ihgfa*. For Hg atoms, a wide spectrum of coordination number (CN) values was established: 11 (5 atoms), 12 (8 atoms), and 13 (1 atom). Ca atoms exhibited the CN of 14 (1 atom), 15 (2 atoms), and 16 (1 atom).

In the present study, we performed the geometric and topological analysis of the crystal structure of the intermetallide Ca$_{11}$Hg$_{54}$–*hP*65 by the ToposPro software package [10]. The symmetry and topological code for the processes of self-assembly of the 3D structure from precursor clusters K46 were simulated in the following form: primary chain → microlayer → microframework.

The present study represents a followup to the works [7, 8, 11–16] in the field of simulation of the processes of self-assembly of systems on the suprapolyhedral scale and the geometrical and topological analysis of crystal structures by advanced computer methods.

Table 1. Crystallographic data

Compound	Hg/Ca	Structure type	No of compounds [1]	Space group	Class Pearson	Cell parameters, Å	V, Å^3
Ca_3Hg [2]	0.33	Fe_3C	194	*Pnma* (62)	oP16	8.161, 10.150, 6.828	565.6
Ca_3Hg [3]	0.33	Cu_3Au	1827	*Pm*-3*m* (221)	CP4	4.920, 4.920, 4.920	119.1
Ca_2Hg [2]	0.5	Co_2Si	43	*Pnma* (62)	OP12	7.860, 4.890, 9.870	379.4
Ca_5Hg_3 [2]	0.6	Cr_5B_3	183	*I*4/*mcm* (140)	tI32	8.189, 8.189, 14.701	985.8
Ca_3Hg_2 [2]	0.66	U_3Si_2	142	*P*4/*mbm* (127)	tP10	8.476, 8.476, 4.197	301.5
Ca_2Hg_2 [2]	1	CsCl	1797	*Pm*-3*m* (221)	CP2.	3.759, 3.759, 3.759	53.1
$CaHg_2$ [2]	2	Alb_2	43	*P*-3*m 1*(164)	hP3	4.894, 4.894, 3.571	74.1
Ca_4Hg_9 [4]	2.25	Cu_9Al_4	47	*P*-43*m* (215)	cP52	11.130, 11.130, 11.130	1378.8
$CaHg_3$ [2]	3	Mg_3Cd	356	*P*6$_3$/*mmc* (194)	hP8	6.635, 6.635, 5.020	191.4
$Ca_{11}Hg_{54}$ [5]	4.90	$Ca_{11}Hg_{54}$	3	*P*-6 (174)	hP65	13.389, 13.389, 9.615	1492.7
$CaHg_{11}$ [6]	11	$BaHg_{11}$	13	*Pm*-3*m* (221)	cP36	9.600, 9.600, 9.600	884.7

COMPUTER ANALYSIS METHODS

The geometrical and topological analysis was performed by means of the ToposPro software package [10], which made it possible to conduct a multipurpose study of the crystal structure automatically, using the representation of structures in the form of "folded graphs" (factor graphs). The data on the functional role of atoms in the formation of a crystalline structure were obtained by calculating coordination sequences, i.e., sets of numbers $\{N_k\}$, where N_k was the number of atoms in the *k*th coordination sphere of a given atom.

Table 2. Local surrounding of Ca and Hg atoms and values of coordination sequences

Atom	Local surrounding	Coordination sequences				
		N_1	N_2	N_3	N_4	N_5
CA1	14Hg	**14**	47	106	189	312
Ca2	15HG	**15**	48	104	190	312
CA3	15HG	**15**	47	105	200	310
CA4	1Ca + 15Hg	**16**	46	104	193	310
Hg2	4Ca + 8Hg	**12**	47	106	189	294
Hg3	3Ca + 8Hg	**11**	46	104	187	290
Hg4	2Ca + 11Hg	**13**	47	108	188	297
Hg5	3Ca + 9Hg	**12**	47	108	189	302
Hg6	3Ca + 9Hg	**12**	47	103	190	299
Hg7	4Ca + 8Hg	**12**	48	104	192	302
Hg8	4Ca + 8Hg	**12**	47	109	193	309
Hg9	1Ca + 11Hg	**12**	46	106	192	303
HG10	3Ca + 9Hg	**12**	46	105	194	316
Hg11	3Ca + 9Hg	**12**	44	109	194	313
Hg12	3Ca + 8Hg	**11**	44	101	188	302
Hg13	3Ca + 8Hg	**11**	47	107	191	299
Hg14	3Ca + 8Hg	**11**	44	107	182	305
Hg15	11Hg	**11**	47	107	188	302

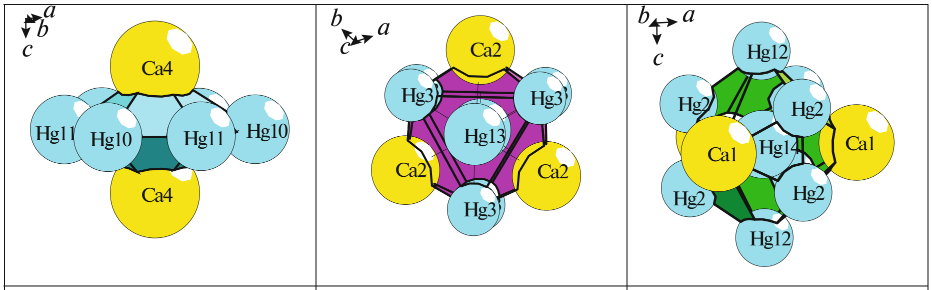
The obtained values of the coordination sequences of atoms in the 3D lattices are provided in Table 2, in which the number of neighboring atoms in the most proximate surrounding, i.e., in the first coordination sphere of the atom, was separated. All atoms were characterized by different sets of the coordination sequences $\{N_k\}$; therefore, all the atoms were topologically (and functionally) different.

The algorithm for automatic decomposition of a structure of any intermetallide, represented in the form of a folded graph, onto cluster units was based on the following principles: a structure was formed as a result of self-assembly from precursor clusters. Here, the precursor clusters formed a structure framework, voids in which were filled with spacer clusters (consisting of a small number of atoms), the precursor nanoclusters did not have shared internal atoms; however, they could have shared atoms on the surface, the precursor clusters occupied highly symmetric positions and the set of precursor nanoclusters and spacer clusters included all atoms of the structure.

The algorithm was implemented by the ToposPro software package [10].

SELF-ASSEMBLY OF THE CRYSTAL STRUCTURE OF $Ca_{11}Hg_{54}$–*hP*65

The method of simulation of the crystal structure that we used was based on determining the hierarchical sequence of its self-assembly in the crystallographic space [11]. At the first level of the system self-assembly, the mechanism of formation of a primary chain of the structure from 0-level nanoclusters formed at the template stage of the chemical evolution of the system is determined, then the mechanism of self-assembly from the layer chain (2nd level), and, thereafter, from the layer of three-dimensional framework (3rd level).



$K8 = 0@Ca_2Hg_6$ $K11 = 0@Ca_3Hg_8$ $K12 = Hg(Ca_3Hg_8)$

Fig. 1. Polyhedral clusters.

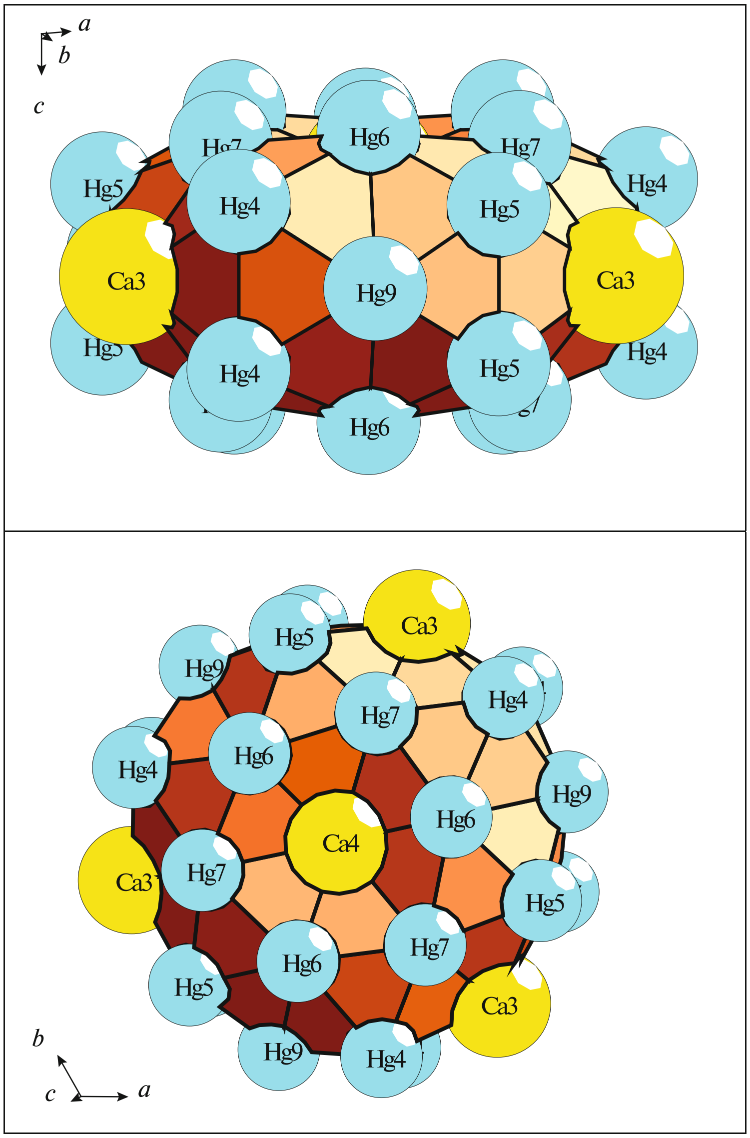


Fig. 2. Cluster K46 (two projections).

Crystallographic data. Parameters of the hexagonal cell: $a = b = 13.389$, $c = 9.615$ Å.

Space group P-6 (no. 174) with elements of the point symmetry: $g = -6$ (1a, 1b, 1c, 1d, 1e, 1f), 3 (2g, 2h, 2i), m (3j, 3k). The order of the group was 6.

Polyhedral clusters K8, K11 and K12. 184 variants of the cluster representation of the 3D atomic lattice with a number of structural units from 3 to 7 was established.

The polyhedral clusters $K8 = 0@Ca_2Hg_6$ which appeared to be hexagonal bipyramids, the polyhedral

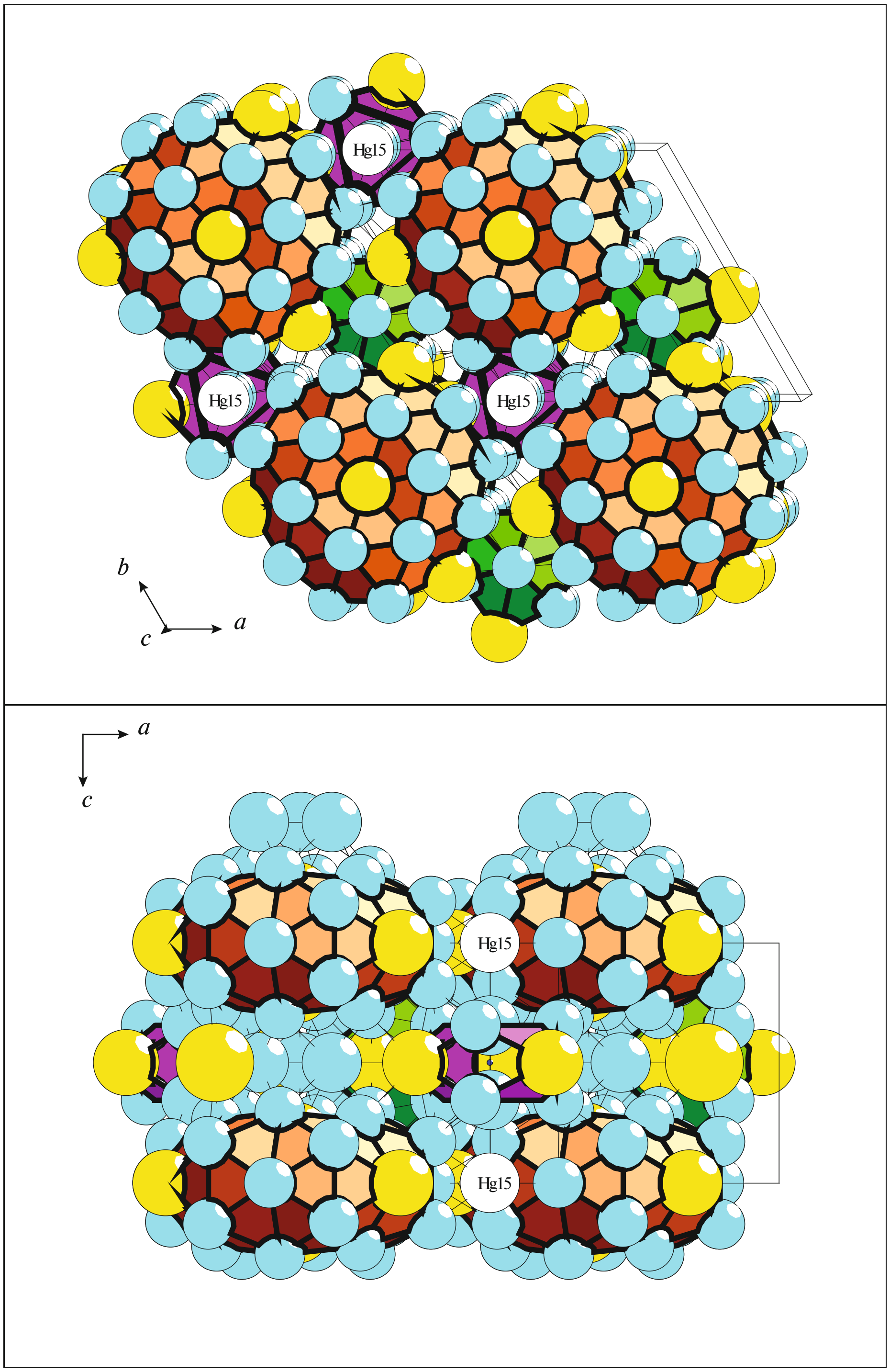


Fig. 3. Framework structure (two projections).

clusters K11 = $0@Ca_3Hg_8$ and the polyhedral clusters with the central Hg atom K12 = Hg (Ca_3Hg_8) were determined (Fig. 1).

The centers of the clusters Ca_2Hg_6, $0@Ca_3Hg_8$ and $Hg(Ca_3Hg_8)$ occupied the most highly symmetric positions 1*c*, 1*b*, and 1*f* with a –6 symmetry.

Suprapolyhedral precursor clusters K46. The clusters Ca_2Hg_6 represented templates, on the surface of which atomic shells were formed of 38 atoms (Fig. 2). The composition of the two-layered cluster K46 was $0@8(Ca_2Hg_6)@38(Hg_6 + CaHg_6)_2(Ca_6Hg_6)$.

Self-assembly of the crystalline structure. Primary chain. The formation of primary chains S_3^1 occured upon binding of K46 clusters by triple Hg_3 rings towards the direction [001]. The distance between the centers of the K46 in the primary chain determined the value of the translation vector $c = 9.818$ Å.

2D layer. The layer S_3^2 was formed upon binding of the primary chains S_3^1 towards the direction [100] (Fig. 3). A distance between the axes of the primary chains determined the value of the translation vector $a = 13.602$ Å. The voids in the framework were occupied by the polyhedral clusters $0@Ca_3Hg_8$ and $Hg(Ca_3Hg_8)$ and the spacer Hg(14) atoms (Fig. 3).

Self-assembly of the framework. The 3D framework structure S_3^3 was formed upon binding of the 2D layers (with a shift) towards the direction [010] (Fig. 3). In the 3D framework, the distance between the equivalent 2D layers determined the value of the vector $b = 13.602$ Å.

CONCLUSIONS

The combinatory-topological analysis and simulation of cluster self-assembly of the $Ca_{11}Hg_{54}$–*hP*65 crystal structure have been performed.

The polyhedral clusters $K8 = 0@Ca_2Hg_6$, which had appeared to be hexagonal bipyramids, the polyhedral clusters $K11 = 0@Ca_3Hg_8$, and the polyhedral clusters with the central Hg atom $K12 = Hg(Ca_3Hg_8)$ have been determined.

The clusters Ca_2Hg_6 represented templates, on the surface of which atomic shells of 38 atoms have been formed. The composition of the two-layered cluster K46 was $0@8(Ca_2Hg_6)@38(Hg_6 + {}_6)_2(Ca_6Hg_6)$.

The symmetry and topological code of the processes of self-assembly of the 3D structures from K46 precursor nanoclusters in the form primary chain → layer → framework have been simulated. The voids between the primary chains have been occupied by the polyhedral clusters $0@Ca_3Hg_8$ and $Hg(Ca_3Hg_8)$, as well as by the Hg spacer atoms.

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