ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2016, Vol. 42, No. 2, pp. 85–95. © Pleiades Publishing, Ltd., 2016.
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Crystal Chemical Analysis of Structures of the Unsaturated Tetraazamacrocyclic Gold(III) Complexes

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Received June 11, 2015

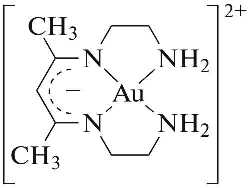
Abstract—The detailed comparative study is carried out for crystal structure packings of the following gold(III) complexes with unsaturated ligands: $[Au(C_{14}H_{22}N_4)]Br$ (**I**), $[Au(C_{14}H_{23}N_4)](ClO_4)_2$ (**II**), $[Au(C_{14}H_{24}N_4)](H_3O)(ClO_4)_4$ (**III**). The determining role in the topological pattern of packings **I–III** belongs to the compositions and structures of the cations along with the ability of the ions of the complexes to act as donors and acceptors of hydrogen bonds. The 3D packings of complexes **I** and **II** containing iminate six-membered rings are determined and stabilized by a wide network of weak hydrogen bonds (C–H···π, C–H···Au, and C–H···Br(O)) and short contacts Au(N)···O (in structure **II**). The structure of imine complex **III** is characterized by one-dimensional piles formed due to hydrogen bonds O(*w*)–H···O and contacts Au···O of the O(2) atom of anion $Cl(1)O_4^-$ with cations $(H_3O)^+$ and $[Au(C_{14}H_{24}N_4)]^{3+}$ (CIF files CCDC 251258 (**I**), 276132 (**II**), and 287784 (**III**)).

DOI: 10.1134/S1070328416020019

INTRODUCTION

We synthesized and studied by physicochemical methods a series of the tetraazametallocyclic gold(III) complexes to the central atom of which nitrogen atoms in different electron states are coordinated (amine $>NH_2$, iminate $>N\overline{\cdots}$, and imine $>N=$) [1]. Both monoatomic (bromide, iodide) and polyatomic (perchlorate, aurite) anions were used as counterions for different complexes. When studying the structures of the synthesized complexes, we considered problems concerning their packing, but no systematic analysis of packings of the complexes depending on the composition and structure of their ions was carried out.

The packings of the acyclic gold(III) iminate–amine complexes $[Au(C_9H_{19}N_4)]Y_2$



with different anions (Y = I, ClO_4, PF_6) were studied in comparison [2]. The influence of substitutions in the β position of the six-membered delocalized ring on the packing of perchlorate complex $[Au(C_9H_{19}N_4)](ClO_4)_2$ was studied [3]. The 3D supramolecular architecture of the crystalline lattice of the acyclic complexes was shown to be determined and stabilized by a wide network of intermolecular interactions (hydrogen bonds and contacts). The decisive role in the formation of structures of the acyclic gold(III) complexes belongs to the planar acyclic cation $[Au(C_9H_{19}N_4)]^{2+}$ providing a potential possibility for the formation of numerous classical and nonclassical cation-cationic and cation-anionic hydrogen bonds. The structure-forming unit of packing in these complexes is presented by doubled cation-anionic piles in which the iminate rings of the heterocycle are localized inside the piles and the amine groups are arranged outside. The cations in the doubled piles are bound due to the cation-cationic hydrogen bonds C–H···π of the delocalized six-membered rings of the cation with the hydrogen atoms of the terminal methyl group of the upper- and lower-lying centrosymmetrical cations. Cavities between the piles contain four infinite chains of anions $Y(1)^-$ and $Y(2)^-$ forming one-dimensional columns of hydrogen bonds and contacts with the amine "tails" arranged outside the piles methylene groups, and central gold atoms linking the doubled piles into cation-anionic 2D layers. A characteristic feature of the crystal structure packings of complexes $[Au(C_9H_{19}N_4)]Y_2$ is the presence of infinite planar ribbons of alternating cations and anions in the 2D layers. In these ribbons, the bridging $Y(1)^-$ and $Y(2)^-$ anions bind the "head" and "tail" of the cations to form closed polymembered rings using cation-anionic hydrogen bonds, and the cations in the layers are parallel to each other. The 2D layers are bound to

Table 1. Selected crystallographic characteristics and refinement parameters for structures **I–III***

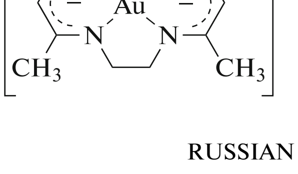
Parameter	Value		
	I	**II**	**III**
Empirical formula	$C_{14}H_{22}N_4BrAu$	$C_{14}H_{23}N_4O_8Cl_2Au$	$C_{14}H_{27}N_4O_{17}Cl_4Au$
FW	386.03	503.15	670.88
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/n$
a, Å	12.592(2)	7.693(1)	11.158(2)
b, Å	6.309(1)	17.366(2)	8.243(1)
c, Å	19.628(2)	15.172(2)	14.756(2)
β, deg	98.00(1)	96.82(1)	98.65(1)
V, Å^3	1544.1(4)	2012.6(4)	1341.8(3)
Z; ρ_{calcd}, g/cm^3	4; 2.251	4; 2.123	2; 1.134
μ, mm^{-1}	12.11	7.626	5.965
Number of reflections with $I > 2\sigma(I)$	1037	2240	1558
Number of refined parameters	99	273	192
R factor, $I > 2\sigma(I)$ R_1	0.0266	0.0352	0.0257

* CIF files CCDC 251256 (**I**) [7], 276132 (**II**) [4], and 287784 (**III**) [6].

each other by cation-anionic nonclassical hydrogen bonds C–H···A (A = I, O, F) of the methyl and methylene groups. Neither the replacement of the anion, nor proton substitution in the β position of the six-membered delocalized ring by hydrogen basically changes the packing. Its characteristic features (doubled piles of cations and chains of anions along the short axis) remain the former, as well as a set of secondary interactions (hydrogen bonds N–H···A, C–H···A, C–H···Au, and C–H···π and short Au···A contacts) that determine and stabilize the packing. The geometry of local fragments joined by hydrogen bonds also remains unchanged.

In this work, we compare the packings of the tatraazamacrocyclic unsaturated gold(III) complexes, [Au(L)]Br (**I**), $[Au(HL)](ClO_4)_2$ (**II**), and $[Au(H_2L)](H_3O)(ClO_4)_4$ (**III**), where L = $C_{14}H_{22}N_4$, in order to reveal regularities of their crystal structures and elucidate the influence of the protonation of the six-membered rings of the ligand on the packing and the role of the ions of the complexes in packing formation.

In an aqueous solution, tetraazamacrocyclic complex $[Au(L)]^+$



(L = $C_{14}H_{22}N_4$) undergoes two-step protonation via reactions (1) and (2)

$$[Au(L)]^+ + H^+ = [Au(HL)]^{2+}, \quad (1)$$

$$[Au(HL)]^{2+} + H^+ = [Au(H_2L)]^{3+} \quad (2)$$

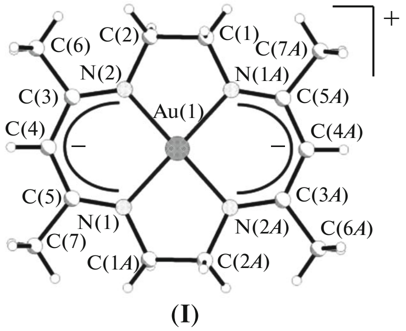
to form mono- and diprotonated forms of the complex: $[Au(HL)]^{2+}$ and $[Au(H_2L)]^{3+}$, respectively [4]. Two protons add consecutively to the central carbon atoms of two six-membered unsaturated rings of the macrocycle, resulting in charge neutralization on the ring, shift of the multiple bonds of the six-membered rings, and localization of π electrons on the C=N bond. The formed mono- and diprotonated complexes contain the negative single-charge iminato–imine (monoprotonated complex) and neutral diimine (diprotonated complex) ligands. The overall charge of the macrocycle increases from +1 to +3, and the central carbon atom of the six-membered imine ring adopts the *sp*^{3} configuration. The diprotonated complex crystallizes only as a double salt with perchloric acid containing a proton in the oxonium form H_3O^+.

Bromide salt of tetraazamacrocyclic complex **I** and perchlorate salts of its mono- and diprotonated forms **II** and **III** were isolated and characterized by the chemical and physical methods [4–7]. The X-ray diffraction analysis data for them were obtained, but a detailed analysis of their packings is lacking.

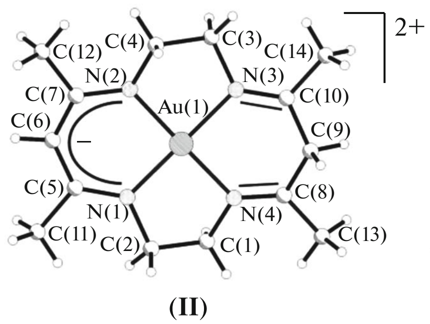
DESCRIPTION OF CRYSTAL STRUCTURES

Complexes **I–III** have different unit cell parameters and space groups. Their monoclinic crystals are not isostructural (Table 1). The crystal structures of complexes **I–III** are ionic and consist of discrete cations and anions.

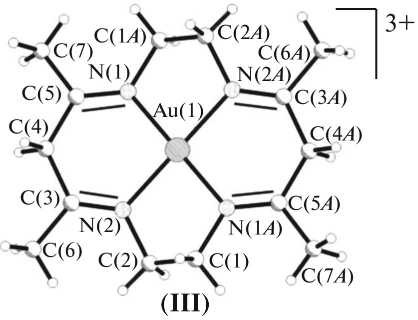
Each 14-membered heterocyclic cation of complexes **I–III** contains two five-membered rings with saturated C–C and C–N bonds and two six-membered unsaturated rings, and two methyl groups in the α position of the heterocycle are attached to each ring



(I)



(II)



(III)

The coordination sphere of each gold atom in complexes **I–III** contains four nitrogen atoms (Au–N 1.967(7)–1.996(5) Å, angles NAuN 84.0(3)°–96.1(3)°). The coordination squares AuN_4 are nearly planar, and the N–N distances are 2.661–2.685 and 2.937–2.950 Å.

The six-membered iminate rings in complexes **I** and **II** include C and N atoms in the sp^2 state and formally contain two double bonds and a negative charge. The C–N (1.303(9)–1.35(1) Å) and C–C (1.38(1)–1.408(10) Å) bond lengths are intermediate between those of ordinary and double bonds [8]. The rings are nearly planar (the maximum deviations of the atoms from their mean-square planes are 0.046 Å (**I**) and 0.033 (**II**) Å) and have a weak inflection along the line connecting two iminate carbon atoms (6.6° (**I**) and 8.6° (**II**)).

In the protonated six-membered rings of cations **II** and **III**, and C–N bond lengths (1.25(1)–1.288(7) Å) indicate the localization of π electrons with the formation of diimine bonds. The C–C distances (1.477(9)–1.500(9) Å) correspond to ordinary bonds. Upon ring protonation they adopt a conformation close to a distorted boat, and the dihedral angle between the CCNNAu and CCC planes is equal to 20°.

The five-membered ethylenediamine rings of complexes **I–III** have a usual *gauche* conformation as in the most part of complexes with ethylenediamine bridges and bidentate-chelating En ligands.

As a whole, cations **I–III** are planar. Protonation leads to some increase in the mean-square deviation of the non-hydrogen atoms from the planes of the cations (Δ = 0.102, 0.117, and 0.155 Å for **I**, **II**, and **III**, respectively).[1]

The detailed analysis of the structures of complexes **I–III** suggests that the packings of the complexes have common structural units and specific features caused by differences in the electronic states of the nitrogen atoms coordinated to the central gold atom.

The projection of the crystal structure of diiminate complex **I** [7] onto the plane (110) is presented in Fig. 1a. A characteristic feature of packing **I** is the presence of cationic layers perpendicular to axis *c* (at $z = 0$ and 0.5). The adjacent cationic layers multiplied by plane *c* are unfolded relatively to each other by 69°. The chains of unbound anions Br^- are extended in the direction [110] between the cationic layers at $z = 0.25$ and 0.75.

The cationic layers in structure **I** (Fig. 2a) can be presented as a set of piles of cations translationally identical in the direction [110]. The piles are bound into the 2D layer by interactions C–H···π [9–11] of the H(72) and H(73) atoms of the bridging methyl groups $C(7)H_3$ of the cation with π-electron clouds of the delocalized six-membered rings of the upper- and lower-lying cations[2] (Table 2). As a result, each cation participates in the formation of four chains of two independent hydrogen bonds C–H···π. The cations of the piles are also bound in the direction [110] by cation-cationic hydrogen bonds C–H···Au of the methyl groups $C(7)H_3$ with the central Au atoms of the upper- and lower-lying cations of the adjacent piles to form nearly planar (Δ = 0.0737 Å) cation-cationic chains ···Au(1')···H(72)–C(7)–H(73)···Au(1'')···. The cations of the layer are parallel to each other and involved in the formation of "pseudo-ribbons" composed of the cations extended in the direction [–130]. The Au···Au distance in the ribbons is 11.37 Å. The Br^-

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[1] The mean-square deviation (Δ) of non-hydrogen atoms from the cation plane was calculated ignoring the methyl carbon atoms.

[2] The geometry of the C–H···π interactions in the acyclic gold(III) complexes was discussed in [2]. In Figs. 1a, 1b, 2a, and 2b, hydrogen bonds C–H···π are omitted.

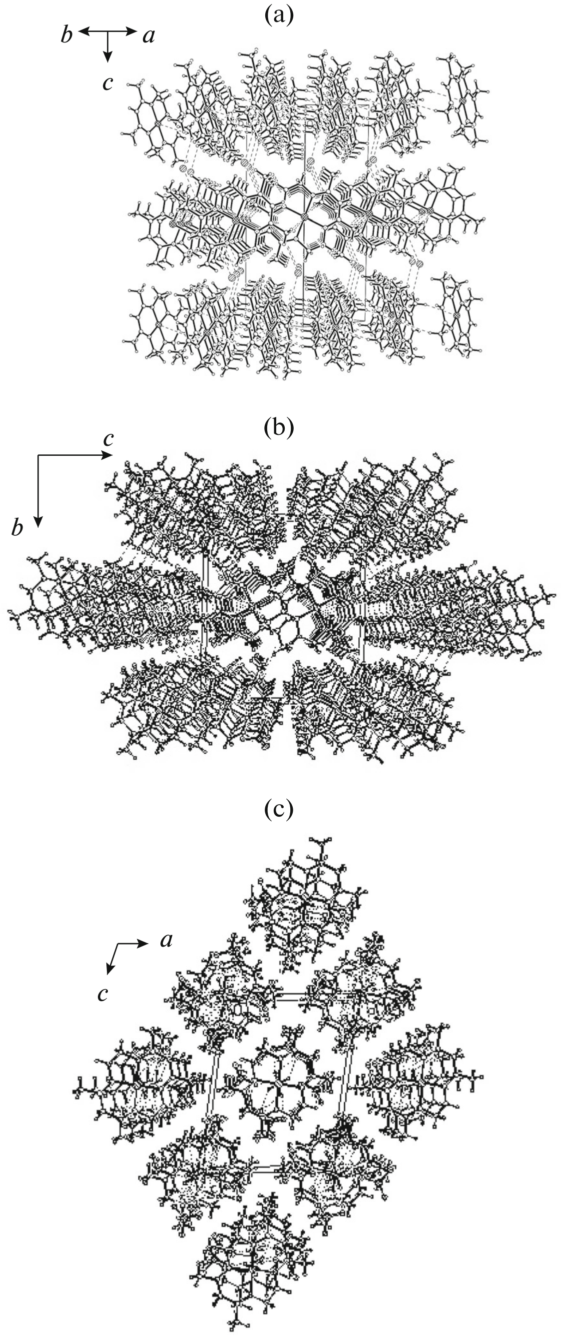

Fig. 1. Crystal structures projected onto the planes (a) (110) in **I**, (b) (100) in **II**, and (c) (010) in **III**.

anions ($\Delta = 0.102$ Å)[3] lie in the plane of each "pseudo-ribbon."

The Br^-anions are bridging in the cation-anionic chains –Au(1')–N(1')–C(5')–C(7')–H(71')···Br(1)···H(71)–C(7)–C(5)–N(1)–Au(1)– (Fig. 3a), binding the cationic layers between each other and forming the 3D structure. These zigzag chains are extended in the direction [101] and have planar fragments (for C(7')H(71')Br(1)H(71)C(7), $\Delta = 0.0403$ Å). The angle between the hydrogen bonds formed by the anion is 138°. The cation-anionic 2D network demonstrating the binding of the layers (Fig. 3a) contains rings of two types: cation-cationic (formed by the hydrogen bonds C–H···Au of two cations) and cation-anionic (including two hydrogen bonds C–H···Au and four hydrogen bonds C–H···Br formed by four cations and two anions).

Thus, each cation in structure **I** participates in the formation of four cation-cationic chains of the hydrogen bonds C–H···π and four cation-cationic chains of the C–H···Au bonds in the direction [110], as well as one cation-anionic chain of the hydrogen bonds C–H···Br in the direction [101]. Note that only two methyl groups $C(7)H_3$ of the cation bound by the symmetry center are involved in hydrogen bond formation, whereas the $C(6)H_3$ methyl groups and the $>CH_2$ and –CH groups of the cation form no hydrogen bonds. The hydrogen atoms of the bridging $C(7)H_3$ groups perform different functions: the H(72) and H(73) atoms link the cations into layers, whereas the H(71) atoms form hydrogen bonds between the layers.

As a whole, the packing of complex **I** is formed and stabilized due to weak secondary interactions (hydrogen bonds) binding the cations and anions into chains and rings to form an infinite 3D network. The donors of the hydrogen bonds are the methyl groups of the cations, whereas the delocalized rings, central atoms of the cations, and anions serve as acceptors. The main structure-forming role in the packing of crystal **I** belongs to the cations that manifest both the donor and acceptor properties.

The packing structure of monoprotonated complex **II** [4] (Fig. 1b) consists of doubled piles of the cations extended in the direction of the short axis *a*, and four chains of the anions are located at the periphery of the piles.

The cations in the doubled piles (Fig. 2b) are bound by symmetry centers, the iminate rings are located inside the piles, and the imine rings are arranged outside the piles. The hydrogen atoms of the terminal methyl groups $C(11)H_3$ of the iminate rings of the cation form with the upper- and lower-lying cations of the double pile cation-cationic hydrogen bonds C–H···π (Table 2). As a result, in the direction of axis *a* each cation is penetrated by two infinite chains of two independent cation-cationic hydrogen bonds C–H···π. The cations in the doubled pile are also bound in pairs by the almost linear (166°) cation-cationic nonclassical hydrogen bond C(11)–H(11)···Au to form nearly planar ($\Delta = 0.0691$ Å) cation-cationic

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[3] The mean-square deviation (Δ) was calculated taking into account the atoms of two coordination sites AuN_4 of the cations and four Br^- anions lying in the plane of the "pseudo-ribbon." In Fig. 2a, anions Br^- are omitted.

Table 2. Geometric parameters of hydrogen bonds and contacts in structures **I–III**

D–H···A	Distance, Å			Angle DHA, deg	Symmetry transform for A
	D···A	H···A	D–H		
		I			
		C—H···Br			
C(7)—H(71)···Br(1)	3.722(8)	2.91	0.96	144	x, y, z
		C—H···Au			
C(7)—H(72)···Au(1)	4.118(9)	3.16	0.96	174	$1 - x, -y, 1 - z$
C(7)—H(73)···Au(1)	3.957(8)	3.06	0.96	156	$0.5 - x, -0.5 - y, 1 - z$
		C—H···π			
C(7)—H(72)···N(1)	3.959(10)	3.19	0.96	138	$1 - x, -y, 1 - z$
C(7)—H(72)···C(3)	3.595(10)	3.01	0.96	121	$1 - x, -y, 1 - z$
C(7)—H(72)···C(4)	3.679(11)	3.18	0.96	114	$1 - x, -y, 1 - z$
C(7)—H(72)···C(5)	3.833(11)	3.26	0.96	121	$1 - x, -y, 1 - z$
C(7)—H(72)···N(2)	3.698(10)	2.90	0.96	141	$1 - x, -y, 1 - z$
C(7)—H(72)···L(1)*	3.485(9)	2.70	0.96	139	$1 - x, -y, 1 - z$
C(7)—H(73)···C(3)	3.708(11)	3.21	0.96	114	$0.5 - x, -0.5 - y, 1 - z$
C(7)—H(73)···N(2)	3.595(10)	2.83	0.96	137	$0.5 - x, -0.5 - y, 1 - z$
C(7)—H(73)···L(1)*	3.685(8)	3.05	0.96	125	$0.5 - x, -0.5 - y, 1 - z$
		II			
		C—H···O			
C(1)—H(1)···O(5)	3.34(2)	2.57	0.98	137	x, y, z
C(9)—H(9)···O(2)	3.14(1)	2.44	0.98	128	x, y, z
C(12)—H(12)···O(7)	3.42(2)	2.53	0.98	155	$1 - x, -0.5 + y, 0.5 - z$
		C—H···Au			
C(11)—H(11)···Au(1)	4.24(1)	3.30	0.96	166	$2 - x, -y, -z$
		C—H···π			
C(11)—H(11)···N(1)	3.97(1)	3.19	0.96	140	$2 - x, -y, -z$
C(11)—H(11)···N(2)	4.09(1)	3.38	0.96	132	$2 - x, -y, -z$
C(11)—H(11)···C(5)	3.93(1)	3.37	0.96	120	$2 - x, -y, -z$
C(11)—H(11)···C(6)	3.93(1)	3.49	0.96	111	$2 - x, -y, -z$
C(11)—H(11)···C(7)	3.99(2)	3.49	0.96	115	$2 - x, -y, -z$
C(11)—H(11)···L(1)*	3.71(1)	2.99	0.96	133	$2 - x, -y, -z$
C(11)—H(11)···N(2)	3.76(1)	2.98	0.96	140	$1 - x, -y, -z$
C(11)—H(11)···C(7)	3.97(2)	3.45	0.96	117	$1 - x, -y, -z$
C(11)—H(11)···L(1)*	4.14(1)	3.54	0.96	123	$1 - x, -y, -z$
		Contacts			
Au(1)···O(6)	3.272(13)				x, y, z
N(4)···O(8)	2.706(10)				$1 + x, y, z$
N(3)···O(6)	2.919(13)				x, y, z
		III			
		O(*w*)—H···O			
O(1*w*)– H(2*w*)···O(2)	2.566(6)	1.58	0.99	177	$x, 1 + y, z$
O(1*w*)– H(7*w*)···O(7)	2.933(10)	1.95	0.99	170	x, y, z
O(1*w*)– H(7*w*)···O(8)	2.868(12)	2.34	0.99	113	x, y, z
O(1*w*)– H(8*w*)···O(8)	2.868(12)	2.02	0.98	144	$-x, 1 - y, -z$
		Contacts			
Au(1)···O(2)	2.980(6)				x, y, z

* L(1) is the midpoint of the six-membered rings of the complex cation.

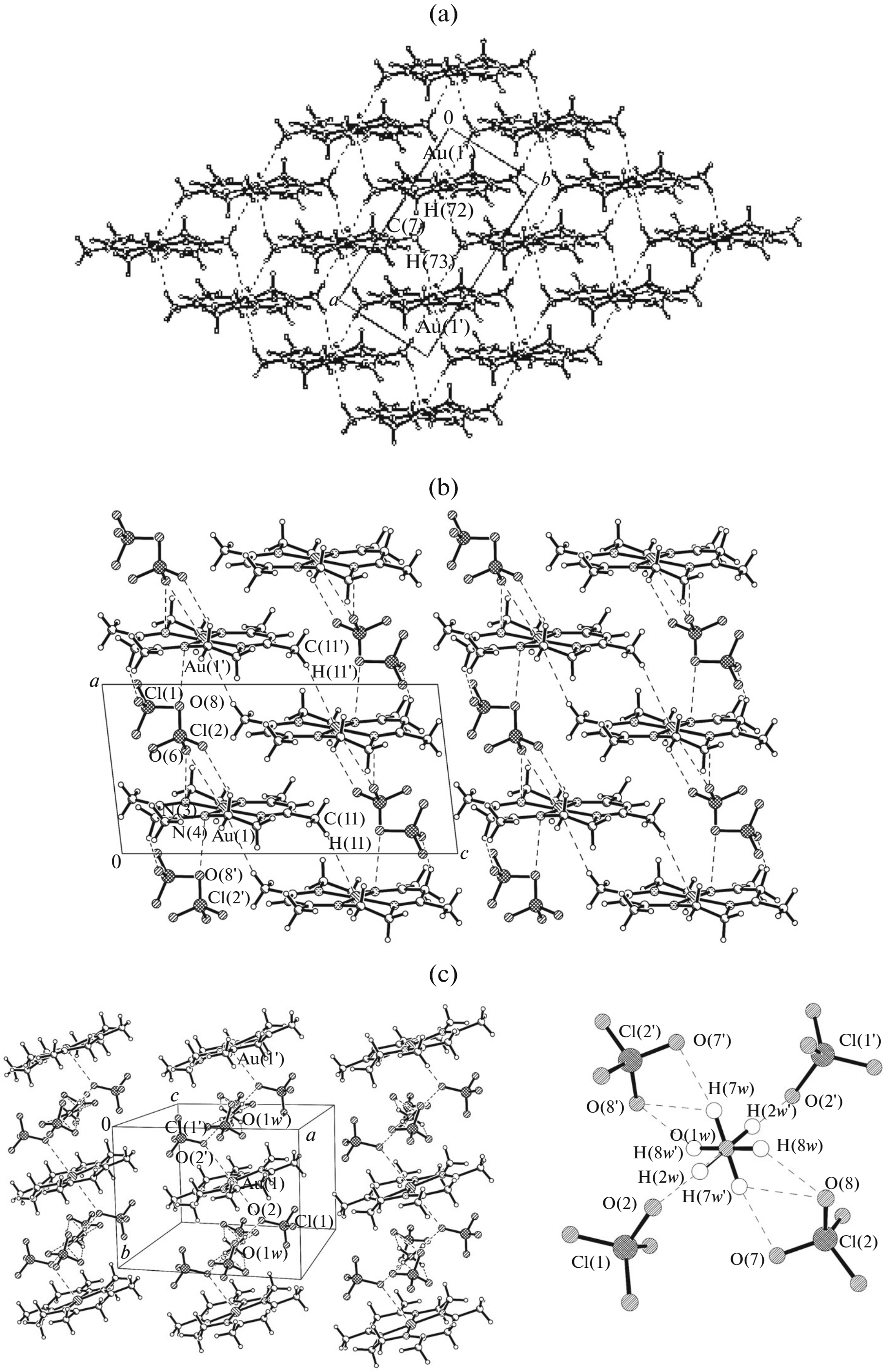

Fig. 2. (a) Projection of the cationic layer onto the plane (001) in **I**. Cation-anionic "pseudo-layers" (b) in **II** (projection onto the plane (010)) and (c) in **III** (projection onto the plane (001).

rings. Note that the methyl groups of the imine rings form no hydrogen bonds.

The imine rings of the translationally identical cations of the doubled piles are linked due to short contacts of the N(3) and N(4) atoms with the O(6) and O(8') atoms of the upper- and lower-lying bridging anions $Cl(2)O_4^-$ to form vertical cation-anionic chains (Fig. 2b). The N(3)···O(6) contact is enhanced by the C(1)–H(1)···O(5) hydrogen bond (Table 2) and the Au(1)···O(6) contact supplementing the coordination number of the gold atom to five (the slope angle of the Au···O vector to the plane of the cation is 56.8°). The Au···O (3.272(13) Å) and N···O (2.706(10) and

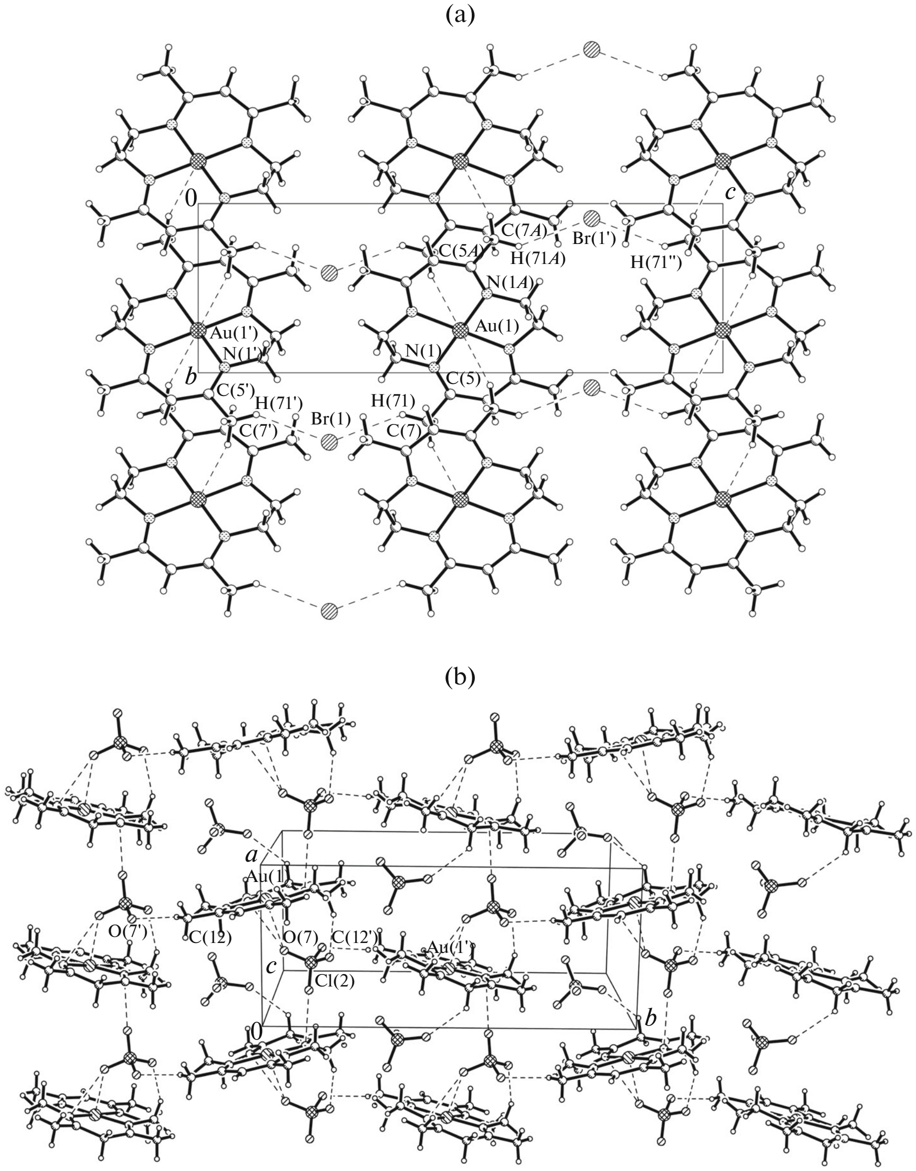

Fig. 3. Fragments of the crystal packings in structures (a) **I** (projection onto the plane (100)) and (b) **II** (projection onto the plane (001)).

2.919(13) Å) contacts are substantially smaller than the sum of the van der Waals radii of the corresponding atoms (3.5 and 3.1 Å) [12].

The translationally identical doubled cation-anionic piles in the direction *c* form "pseudo-layers" (Fig. 2b) with parallel macrocyclic cations and almost planar cation-anionic "pseudo-ribbons" (Δ = 0.12 Å).[4] The Au···Au distance in the ribbons is 15.172(2) Å. The central gold atoms of the cations of each "pseudo-layer" lie in one plane (Δ = 0.01 Å). The adjacent "pseudo-layers" are connected to each other by the sliding plane *n* and are unfolded relatively to each other by 155°.

In the directions [010], [011], and [0$\bar{1}$1], the doubled cation-anionic piles are related to each other by weak cation-anionic interactions of the methyl groups $C(12)H_3$ of the iminate rings of the cations with the O(7) atoms of the $Cl(2)O_4^-$ anions of four adjacent doubled piles to form cation-anionic 2D networks in each of which cation-anionic chains and rings can be revealed. In particular, the cation-anionic 2D network consisting of cation-anionic rings of three types in the projection onto the plane (001) is presented in Fig. 3b.

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[4] The mean-square deviation (Δ) was calculated taking into account the atoms of two coordination sites AuN_4 of the cations and the central atoms of two pairs of anions $Cl(1)O_4^-$ and $Cl(2)O_4^-$ of the "pseudo-ribbon."

Table 3. Variants of the most symmetrical translational sublattices in structures **I–III**

Compound	**I**	**II**	**III**
Empirical formula	$C_{14}H_{22}N_4BrAu$	$C_{14}H_{23}N_4O_8Cl_2Au$	$C_{14}H_{27}N_4O_{17}Cl_4Au$
h_1, k_1, l_1	2 0 2	0 1 1	$0\ 1\ \bar{1}$
h_2, k_2, l_2	1 1 1	$0\ \bar{1}\ 1$	$0\ \bar{1}\ \bar{1}$
h_3, k_3, l_3	0 0 2	2 0 0	$\bar{1}\ 0\ 1$
Δ	4	4	2
a_T, Å	7.04	11.53	9.50
b_T, Å	6.31	11.53	9.50
c_T, Å	12.38	3.85	11.16
α_T, deg	90.0	94.5	61.9
β_T, deg	123.6	94.5	61.9
γ_T, deg	116.6	97.7	51.5
$\boldsymbol{a}_T$	$\boldsymbol{a}/2 - \boldsymbol{b}/2$	$\boldsymbol{b}/2 + \boldsymbol{c}/2$	$\boldsymbol{a}/2 - \boldsymbol{b}/2 + \boldsymbol{c}/2$
$\boldsymbol{b}_T$	$\boldsymbol{b}$	$-\boldsymbol{b}/2 + \boldsymbol{c}/2$	$-\boldsymbol{a}/2 - \boldsymbol{b}/2 - \boldsymbol{c}/2$
$\boldsymbol{c}_T$	$-\boldsymbol{a}/2 + \boldsymbol{c}/2$	$\boldsymbol{a}/2$	$\boldsymbol{a}$

The 2D networks are realized in several directions, indicating the 3D structure of complex **II**.

The structure-forming units of complex **III**, whose molecular formula contains the macrocyclic cation $[Au(C_{14}H_{24}N_4)]^{3+}$, oxonium cation H_3O^+, and four anions ClO_4^-, are cation-anionic piles extended in the direction of axis *b* (Fig. 1c) [6]. The piles consist of alternating translationally identical macrocyclic cations and oxonium cations in the environment of four perchlorate anions (Fig. 2c). The distance between the centers of cations in the pile is equal to *b*/2. Note that the central atoms of the oxonium cations and perchlorate anions lie in the plane (Cl(1)Cl(2)O(1*w*)Cl(1')Cl(2')) nearly parallel to the macrocyclic cation plane (the dihedral angle between the planes is 6°).

The disordered oxonium ion forms a system of hydrogen bonds O(*w*)–H···O [6] with four anions (Fig. 2c, at the right). The H(2*w*) atom forms an almost linear (177°) hydrogen bond O(1*w*)–H(2*w*)···O(2) with the anion $Cl(1)O_4^-$. The H(7*w*) atom forms a planar three-center hydrogen bond O(1*w*)–H(7*w*')···O(7), O(8) (Δ = 0.021 Å). The whole oxonium ion is involved in the planar "chelate" hydrogen bond O(8)···H(7*w*')–O(1*w*)–H(8*w*)···O(8) (Δ = 0.009 Å) with the anion $Cl(2)O_4^-$; and both three-centered and "chelate" hydrogen bonds lie in one plane (Δ = 0.020 Å). Structure **III** is an example of a combination of the three-centered and "chelate" hydrogen bonds taking place in crystal structures of amino acids and inclusion compounds [13] and in the structure of the studied by us iminate–amine iodide complex $[Au(C_9H_{19}N_4)]I_2$ [14].

The diprotonated macrocyclic cation $[Au(C_{14}H_{24}N_4)]^{3+}$ forms no hydrogen bonds (unlike deprotonated **I** and monoprotonated **II**) and has only two short (2.98 Å for the sum of the van der Waals radii equal to 3.5 Å) contacts of the central gold atom with the bound by the symmetry center O(2) and O(2') atoms of the upper- and lower-lying anions $Cl(1)O_4^-$, supplementing the coordination number of the gold atom to six (Fig. 2c); i.e., the O(2) atom is bridging and links the $[Au(C_{14}H_{24}N_4)]^{3+}$ and H_3O^+ cations into a chain in the direction of axis *b*. The slope angle of the Au···O vector to the cation plane is 68°.

The cation-anionic piles in structure **III** are not linked to each other, so that structure **III** can be characterized as a 1D chain structure. Nevertheless, the characterization of the packing indicates "pseudo-layers" in structure **III** as in structure **II**. The "pseudo-layers" are parallel to the planes (100) and (001) and extended in the directions *c* and *a*, respectively. The "pseudo-layer" projected onto the plane (001) is shown in Fig. 2c. The cations of the "pseudo-layer" are parallel to each other. The "pseudo-ribbons" extending in the direction $[2\bar{1}0]$ are planar (Δ = 0.076 Å),[5] and the Au···Au distance in the ribbons is 23.79 Å. The adjacent "pseudo-layers" multiplied by plane *n* are remote from each other at *a*/2 and *c*/2, respectively. The cations of the adjacent "pseudo-layers" are inclined to each other by 38.8°.

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[5] The mean-square deviation (Δ) of non-hydrogen atoms from the plane of the "pseudo-ribbon" was calculated taking into account two coordination sites AuN_4 of the macrocyclic cations and the central atoms of two oxonium cations in the planar-square environment of the perchlorate anions.

When describing the structure of tetraazamacrocyclic gold(III) perrhenate complex $[Au(C_{14}H_{22}N_4)]ReO_4$ [15], we established the pseudo-hexagonal motif of the crystal structure using the modified method of translational sublattices for calculations [16]. The essence of the modification, i.e., the construction of the theoretical diffraction using only atoms belonging to the fragment interested in was described [17]. For example, the calculation by the central atoms of the complex cations (taken as those having a larger size) makes it possible to reveal the crystallographic planes that are most populated by these atoms and to study the motif of their mutual arrangement. The theoretical diffraction pattern was calculated in [15] by the Au atoms only. Then possible variants were found using the program [18]. These variants should satisfy the condition $Z = \Delta$, where Z is the number of formula units (or Au atoms) falling per unit cell, and Δ is the determinant of the matrix built of indices of the most intense diffraction reflections.

Using the method of translational sublattices for an analysis of the structures of complexes **I–III**, we obtained variants with the most symmetrical sublattices (Table 3), also indicating pseudo-hexagonal motifs of the arrangement of the central atoms of the cations. In particular, it was found for complex **I** that one of the most symmetrical sublattices was formed by the intersection of families of the planes {2 0 2}, {1 1 1}, and {0 0 2}. The sublattice is built on the vectors $\boldsymbol{a}_t = \boldsymbol{a}/2 - \boldsymbol{b}/2$, $\boldsymbol{b}_t = \boldsymbol{b}$, and $\boldsymbol{c}_t = -\boldsymbol{a}/2 + \boldsymbol{c}/2$. The metrics of the distinguished sublattice are the following: $a_t = 7.04$, $\boldsymbol{b}_t = 6.31$, $\boldsymbol{c}_t = 12.38$ Å, $\alpha_t = 90$, $\beta_t = 123.6$, $\gamma_t = 116.6°$. The pseudohexagonal motif is well seen in the projection of structure **I** in the direction of vector $\boldsymbol{c}$ (Fig. 4): the Au···Au distances range from 6.31 to 7.04 Å, and the AuAuAu angle is close to 120°.

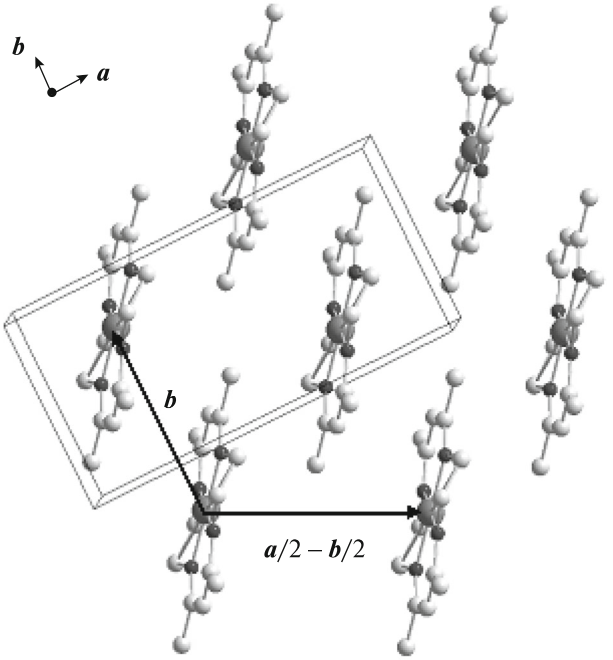

Fig. 4. Fragment of crystal structure **I** as a pseudo-hexagonal layer perpendicular to axis *c*. The vectors of the translational sublattice $\boldsymbol{a}_t$ and $\boldsymbol{b}_t$ are shown, and their lengths correspond to Au···Au distances of 7.04 and 6.31 Å, respectively. Hydrogen atoms are omitted.

RESULTS AND DISCUSSION

The topological pattern of packings of the macrocyclic gold(III) complexes studied in this work, namely, iminate **I**, iminate–imine **II**, and imine **III** (the heterocycle of each complex contains two unsaturated six-membered rings), is similar to that found for the acyclic iminate–amine gold(III) complexes $[Au(C_9H_{19}N_4)]Y_2$ (Y = I, ClO_4, PF_6) with one iminate ring in the heterocycle [2].

In particular, the structure of monoprotonated complex **II** with one iminate ring, as the structures of acyclic complexes $[Au(C_9H_{19}N_4)]Y_2$, consists of doubled cation-anionic piles. The structure of complex **I** is characterized by two-dimensional cationic layers formed due to the presence of two iminate rings in the heterocycle. As in acyclic $[Au(C_9H_{19}N_4)]Y_2$, the cations are bound into layers (**I**) and piles (**II**) due to the chains of hydrogen bonds C–H···π penetrating the iminate rings. The 2D cationic layers in **I** and 1D doubled cation-anionic piles in **II** are joined into a 3D network by the cation-anionic nonclassical hydrogen bonds C–H···A (A = Br, O) of the terminal methyl groups. In acylic complexes $[Au(C_9H_{19}N_4)]Y_2$, the 2D cation-anionic layers are bound by the methylene groups of the ethylenediamine rings along with the methyl groups.

A distinctive feature of the topology of the structure of diprotonated **III** having no delocalized iminate rings is the absence of a binding effect of cations into doubled piles or layers. In complex **III**, π electrons of both six-membered rings are localized on the C=N double bonds, due to which the six-membered rings lose the ability to manifest the acceptor properties for the interactions C–H···π. The 1D cation-anionic piles in **III** are bound only due to the O(2) atoms of the anions $Cl(1)O_4^-$, forming short contacts with the central gold atoms of the macrocycles and hydrogen bonds with the oxonium ions.

Nevertheless, concerning both monoprotonated **II** and diprotonated **III**, we can speak about "pseudo-layer" structures characterized (as in both deprotonated $[Au(C_{14}H_{22}N_4)]Br$ and $[Au(C_9H_{19}N_4)]Y_2$) by parallel macrocyclic cations and planar "pseudo-ribbons" of alternating cations and anions. Unlike the structures of the acyclic complexes [2], the cations and anions of the "pseudo-ribbons" in **I–III** are not linked. The distance between the centers of the macrocyclic cations in the "pseudo-ribbons" of complexes **I–III** increases in the series: iminate (**I**) → iminate–imine (**II**) → imine (**III**) (11.37, 15.17, and 23.79 Å, respectively). The layers in **I** and "pseudo-layers" in **II** and **III** can be presented as both "pseudo-ribbons" multiplied by symmetry centers and a set of doubled (in **II**) or ordinary (in **III**) cation-anionic piles unbound to each other.

The composition and structure of the cations along with the ability of the ions in the complex to act as donors and acceptors of hydrogen bonds play the determining role in the topological pattern of the packings of the heterocyclic unsaturated gold(III) complexes with compact anions, both acyclic compounds [2, 3] and macrocyclic complexes **I–III** studied in the present work.

All hydrogen-containing groups of the ligands in complexes **I–III** (CH_3, CH_2, CH) are localized at the periphery of the cations and are potential donors of weak C–H···A bonds [13, 19]. The oxonium ion in complex **III** is a strong donor of hydrogen bonds O(1*w*)–H···O [13]. The coordinatively unsaturated central gold atom and iminate rings with the π-delocalized electron can exhibit weak acceptor properties [11, 20], and anions Br^- and ClO_4^- are acceptors of strong hydrogen bonds [21].

The planar structure of the macrocyclic gold(III) cations provides a spatial accessibility of the delocalized iminate rings for participation as acceptors in the formation of nonclassical hydrogen bonds C–H···π (in **I** and **II**), and that of the coordinatively unsaturated central Au atom serves for the formation of hydrogen bonds C–H···Au (in **I** and **II**) and contacts Au···O (in **II** and **III**) with the upper- and lower-lying anions.

The methyl groups in the α position of the six-membered rings having a free degree of rotation around the C–C axis are oriented in the structures of complexes **I** and **II** with the iminate rings in such a way that two hydrogen atoms of one methyl group participate in the formation of chains of hydrogen bonds C–H···π binding the cations into doubled piles (in **II**) or into layers (in **I**). Remarkably, the terminal methyl groups exhibit the donor properties only when they are attached to the diiminate ring, and the Me groups of the imine rings are inactive.

The introduction of the strong donor (oxonium ion) into diprotonated complex **III** exerts a significant effect on the structure, substantially changing the system of structure-forming interactions.

According to the empirical Etter rules [22] revealed for crystal structures of neutral organic molecules, all effective donor and acceptor groups are involved in hydrogen bonds with the primary formation of bonds between each other. Weaker donors can form hydrogen bonds only in the presence of excessive (which were not involved in hydrogen bond formation with effective donors) acceptors.

In complexes **I** and **II**, the hydrogen atoms of the methyl and methylene groups (weak donors) form hydrogen bonds with both strong acceptors (anions) and weak acceptors (the central Au atom and delocalized ring of the cation). The bonds of the Me groups with weak acceptors form vertical 1D chains (C–H···π) and cation-cationic rings (C–H···Au) linking cations into doubled piles in structure **II** or into layers in structure **I**. The bonds of the methyl groups with the anions (C–H···Br(O)) join the piles (layers) between each other to form the 3D structure. Structure **III** contains no nonclassical hydrogen bonds, since strong acceptors (anions) prefer to form classical hydrogen bonds with the strong donor (oxonium ion). The 1D cation-anionic piles in structure **III** are formed due to the Au···O contacts.

Thus, in the packings of the crystal structures of the unsaturated macrocyclic complexes **I** and **II**, whose ligands contain iminate six-membered rings, and in the earlier studied acyclic iminate–amine gold(III) complexes [2], the 3D supramolecular architecture of the crystalline lattice is determined and stabilized by a wide network of secondary noncovalent intermolecular interactions (weak nonclassical hydrogen bonds and contacts). Only the pile 1D structure is observed in imine complex **III**. An analysis of the structures of complexes **I–III** using the translational sublattice method indicates the pseudo-hexagonal motif of the arrangement of the central atoms of the macrocyclic cations in the packings regardless of the cation charge.

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Translated by E. Yablonskaya