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Supramolecular Architecture and Regularities of Crystal Packings of the Heterocyclic Gold(III) Iminatoamine Complexes

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Abstract—The regularities of the structural organization of crystal packings in the gold(III) iminatoamine complexes $[Au(C_9H_{19}N_4)]Y_2$ (Y = I, ClO_4, PF_6) and $[Au(C_9H_{18}N_4X)](ClO_4)_2$ (X = Cl, Br) are revealed. The 3D supramolecular architecture of the crystalline lattice of the complexes is characterized by common structural units: 1D cation–anion ribbons (pseudoribbons), cation–cation stacks, and cation–anion columns that form cation–anion layers. The structures of the complexes include infinite chains of hydrogen bonds or contacts containing bridging atoms and closed rings of different dimensionality. The determining role in the topological pattern of packings of the complexes belongs to the planar character of the cation along with the presence of *cis*-amino groups in the AuN_4 coordination node and methyl groups in the α-position of the six-membered delocalized ring. The halogenation of the iminate rings of the ligands does not result in a substantial change in the architecture of the packings.

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INTRODUCTION

In recent decades, chemists working in all areas (from biochemistry to organic, organometallic, and physical chemistry) give rapt attention to secondary noncovalent interactions, which determined the real shift of interest from investigations of atoms and bonds between them to studying molecules and intermolecular bonds. An increasing part of studies is devoted to understanding the nature of intermolecular interactions (hydrogen bonds, short contacts, and other) and the possibility of their use in engineering of organic and organometallic crystals aimed at the design of periodical structures with the desired supramolecular organization [1, 2]. Nevertheless, the reliable prediction of crystal packings continues to be an unsolved problem. Therefore, it is urgent to develop theoretical approaches to the solution of this problem and to analyze empirically crystal-chemical data aimed at establishing structural regularities, whose understanding would make it possible to purposefully construct new functional materials by designing their crystal structures. Hydrogen bonds forming supramolecular motifs most abundant in crystal structures are the most important of all directed intermolecular interactions. Presently, the main section in the investigation of hydrogen bonds is the study of their weak and nonclassical types [3–11] playing a special role in structural chemistry and biology [9, 12].

We synthesized and studied the physicochemical properties of a series of acyclic and macrocyclic (deprotonated and protonated) tetraazagold(III) complexes with nitrogen atoms in different electronic state (amine, $>NH_2$, iminate $>N\overset{...}{-}$, imine >N=) coordinated to the central atom [13]. It seemed reasonable to study the mutual arrangement of ions in packings of the complexes by comparative analysis in order to elucidate regularities of crystal structures of the studied complexes and to reveal the role of cations and anions composing the structures in the formation of the packing and the influence of such factors as the electronic state of the nitrogen atoms in the AuN_4 coordination node, the presence of substituents in the iminate ring of the cation, and the modification of the anion.

The packings of the crystal structures of the gold(III) iminatoamine complexes with single-charged anions $[Au(C_9H_{19}N_4)]Y_2$ (Y = I (**I**), ClO_4 (**II**), and PF_6 (**III**)) were examined [14]. The packing of the complexes is determined and stabilized by secondary noncovalent interactions. When the monoatomic anion is replaced by the polyatomic one, the principal scheme of the packing and characteristic features of its structural fragments are retained but the number of cation–anion bonds N–H···A, C–H···A, and contacts Au···A (A = I, O, F) increases.

In this work, we studied the influence of halogen introduction into the six-membered ring of the $[Au(C_9H_{19}N_4)]^{2+}$ cation on the packing of the gold(III) iminatoamine complexes. The revealed regularities of the supramolecular organization of packings of the gold iminatoamine complexes and geometry of local hydrogen-bonded fragments were formu-

Table 1. Crystallographic characteristics and details of experiments and structure refinement for compounds **II**, **IV**, and **V**

Parameter	**II** [14]	**IV**	**V**
Empirical formula	$C_9H_{19}AuCl_2N_4O_8$	$C_9H_{18}AuCl_3N_4O_8$	$C_9H_{18}AuBrCl_2N_4O_8$
M	579.15	613.59	658.05
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	Cc	$P2_1/c$
a, Å	9.9807(2)	15.8794(5)	20.1171(4)
b, Å	7.0670(2)	13.2209(3)	7.2281(2)
c, Å	23.1451(6)	7.9472(2)	25.2327(6)
β, deg	91.925(1)	94.691(1)	109.327(1)
V, Å^3	1631.59(7)	1662.85(8)	3462.28(14)
Z; ρ(calcd), g/cm^3	4; 2.358	4; 2.451	8; 2.525
μ, mm^{-1}	9.392	9.378	11.162
Crystal sizes, mm	0.17 × 0.15 × 0.09	0.22 × 0.15 × 0.11	0.24 × 0.11 × 0.04
Scan θ range, deg	1.76–25.08	2.01–30.72	1.07–30.76
Number of measured reflections	10960	6083	32045
Number of independent reflections	2887	4588	10619
R(int)	0.0415	0.0111	0.0356
Number of reflections with $I > 2\sigma(I)$	2887	4506	9171
Number of refined parameters	236	229	451
Goodness-of-fit for F^2	1.529	1.016	1.035
R factor, $I > 2\sigma(I)$	$R_1 = 0.0416$	$R_1 = 0.0101$	$R_1 = 0.0269$
	$wR_2 = 0.1108$	$wR_2 = 0.0273$	$wR_2 = 0.0543$
R factor (for all I_{hkl})	$R_1 = 0.0458$	$R_1 = 0.0103$	$R_1 = 0.0360$
	$wR_2 = 0.1169$	$wR_2 = 0.0275$	$wR_2 = 0.0567$
Residual electron density (max/min), e/Å^3	2.518/–1.325	0.485/–0.959	1.714/–1.440

lated. The conclusions about the role of the whole cation and its functional groups in packing formation were made.

EXPERIMENTAL

N,*N'*-Bis(2-aminoethyl)-3-chloro-2,4-pentanediiminatogold(III) bisperchlorate $[Au(C_9H_{18}N_4Cl)](ClO_4)_2$ (**IV**) and *N*,*N'*-bis(2-aminoethyl)-3-bromo-2,4-pentanediiminatogold(III) bisperchlorate $[Au(C_9H_{18}N_4Br)](ClO_4)_2$ (**V**) were synthesized using described procedures [15, 16]. To obtain precision X-ray diffraction data, the unit cell parameters and reflection intensities of single crystals of compounds **IV** and **V** grown from aqueous solutions were measured at a low temperature (150 K)[1] on a Bruker X8 Apex CCD automated diffractometer equipped with a two-coordinate detector using a standard procedure (MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The crystallographic characteristics and details for X-ray diffraction experiments and refinement of structures **IV** and **V** are presented in Table 1. The structures were solved by a direct method and refined by full-matrix least squares

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[1] The X-ray diffraction data for compounds **IV** and **V** obtained at room temperature are published [15, 16].

Table 2. Selected interatomic spacings and bond angles in the structures of compounds **II**, **IV**, and **V***

Bond	**II** [14]	**IV**	**V**	
			K(1)	K(1*A*)
	d, Å			
Au(1)–N(1)	1.976(9)	1.956(7)	1.971(3)	1.984(3)
Au(1)–N(2)	1.982(9)	1.999(6)	1.973(3)	1.971(3)
Au(1)–N(3)	2.036(10)	2.056(7)	2.039(3)	2.040(3)
Au(1)–N(4)	2.046(10)	2.039(7)	2.036(3)	2.047(3)
N(1)–C(5)	1.315(15)	1.408(9)	1.333(4)	1.339(4)
N(1)–C(1)	1.476(15)	1.479(10)	1.488(4)	1.482(4)
N(2)–C(7)	1.326(15)	1.261(9)	1.334(4)	1.331(4)
N(2)–C(3)	1.473(14)	1.478(11)	1.483(5)	1.485(5)
N(3)–C(2)	1.473(17)	1.461(11)	1.496(5)	1.483(5)
N(4)–C(4)	1.484(17)	1.519(10)	1.491(4)	1.490(5)
C(1)–C(2)	1.496(19)	1.436(13)	1.497(5)	1.515(5)
C(3)–C(4)	1.512(18)	1.581(12)	1.510(5)	1.505(5)
C(5)–C(6)	1.392(17)	1.387(11)	1.423(5)	1.409(5)
C(5)–C(8)	1.498(16)	1.566(8)	1.504(4)	1.501(4)
C(6)–C(7)	1.391(16)	1.420(10)	1.404(5)	1.411(5)
C(7)–C(9)	1.507(16)	1.444(9)	1.507(4)	1.499(5)
H(Cl,Br)–C(6)	0.90	1.754(2)	1.912(3)	1.916(3)
Angle	ω, deg			
N(1)Au(1)N(2)	95.1(4)	94.9(1)	95.0(1)	94.5(1)
N(1)Au(1)N(4)	178.7(4)	178.3(3)	177.6(1)	178.6(1)
N(2)Au(1)N(4)	83.7(4)	87.0(3)	84.2(1)	84.7(1)
N(1)Au(1)N(3)	83.0(4)	81.4(3)	84.2(1)	84.6(1)
N(2)Au(1)N(3)	178.9(4)	176.2(3)	179.0(1)	178.3(1)
N(4)Au(1)N(3)	98.2(4)	96.7(1)	96.7(1)	96.3(1)
C(5)N(1)C(1)	122.5(10)	124.3(7)	122.3(3)	122.6(3)
C(5)N(1)Au(1)	123.5(8)	120.9(5)	124.2(2)	124.2(3)
C(1)N(1)Au(1)	113.2(7)	113.4(6)	112.3(2)	111.3(2)
C(7)N(2)C(3)	123.9(10)	121.1(7)	123.1(3)	122.1(3)
C(7)N(2)Au(1)	123.2(8)	127.5(5)	124.0(2)	125.0(3)
C(3)N(2)Au(1)	112.3(7)	109.8(5)	112.0(2)	111.8(2)
C(2)N(3)Au(1)	107.4(8)	107.5(5)	105.1(2)	106.1(2)
C(4)N(4)Au(1)	107.7(7)	106.5(5)	107.7(2)	106.6(2)
C(2)C(1)N(1)	108.3(10)	107.1(7)	108.4(3)	107.9(3)
C(1)C(2)N(3)	108.1(11)	107.9(7)	107.9(3)	107.8(3)
N(2)C(3)C(4)	107.2(10)	108.9(7)	107.2(3)	107.7(3)
N(4)C(4)C(3)	108.3(10)	107.1(5)	107.9(3)	108.8(3)
N(1)C(5)C(6)	124.3(11)	124.4(5)	122.2(3)	122.8(3)
N(1)C(5)C(8)	118.0(11)	113.2(6)	117.6(3)	116.9(3)
C(6)C(5)C(8)	117.7(10)	122.4(5)	120.3(3)	120.2(3)
C(5)C(6)C(7)	129.0(11)	129.4(2)	128.9(3)	128.9(3)
N(2)C(7)C(6)	124.3(11)	121.4(6)	123.2(3)	122.7(3)
N(2)C(7)C(9)	117.8(11)	118.0(6)	115.8(3)	116.6(3)
C(6)C(7)C(9)	117.9(11)	120.4(5)	120.9(3)	120.7(3)
C(7)C(6)H(Cl,Br)	117.9(11)	116.9(4)	116.0(2)	115.7(3)
C(5)C(6)H(Cl,Br)	117.9(11)	113.7(5)	115.1(3)	115.3(3)

* The Cl–O bond lengths and OClO angles of the ClO_4^- anions range from 1.392(6) to 1.444(6) Å and from 106.5(6)° to 114.8(6)° (for **IV**) and from 1.371(5) to 1.448(3) Å and from 108.7(2)° to 113.7(4)° (for **V**), respectively.

for F^2 in the anisotropic approximation for non-hydrogen atoms using the SHELXL-97 program package [17]. Positions of all hydrogen atoms were determined from the difference Fourier syntheses and included into the refinement using the riding model. Selected interatomic spacings and bond angles are given in Table 2. The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (949788 (**IV**) and 949789 (**V**); deposit@ccdc.cam.ac.uk or http://www. ccdc.cam.ac.uk/data_request/cif) and can be available from the authors.

RESULTS AND DISCUSSION

The crystal structures of complexes **IV** and **V** are composed of complex cations $[Au(C_9H_{18}N_4Hal)]^{2+}$ and out-of-sphere perchlorate anions ClO_4^-. Chlorine-substituted complex **IV** has one and two crystallographically independent units for the cation and anions, and bromine-substituted complex **V** has two crystallographically independent cations (K(1) and K(1*A*)) and four crystallographically independent anions. Crystals **IV** and **V** are not isostructural to each other and to unsubstituted perchlorate $[Au(C_9H_{19}N_4)](ClO_4)_2$ (**II**) [14] and have different unit cell parameters and space groups (Table 1). The bond lengths and bond angles of cations $[Au(C_9H_{18}N_4Hal)]^{2+}$ in complexes **IV** and **V** correspond to the values found for the cation $[Au(C_9H_{19}N_4)]^{2+}$ in complex **II** (Table 2).

A comparative analysis of the crystal structure packings of the gold(III) iminatoamine complexes, whose molecular forms contain both different anions and modified (β-substituted) cations revealed the regularities and specific features of their crystal packings and supramolecular architecture.

Figures 1a–1c presents the crystal structures of complexes **IV** and **V** along short axes compared to the structure of complex **II** also containing the ClO_4^- anion. When the covalently bound halogen atoms are introduced into the β-position of the delocalized six-membered ring of the cation, the general scheme of the arrangement of cations and anions is retained but the character of bonds between them changes. If the unsubstituted complexes include cation–anion ribbons formed due to hydrogen bonds of the amine and methyl groups, the character of bonds is different in substituted complexes **IV** and **V**. In particular, in compound **IV**, the cation–anion ribbons from the "head" of the cations are closed by contacts Cl···O (3.174(9) and 3.181(8) Å) (Table 3) rather than by hydrogen bonds C–H···O with methyl groups. In compound **V**, the cation–anion pseudoribbons are not closed. They consist of two independent cation–anion triads linked by the Br···O contact (2.883(1) Å) and the hydrogen bond with the methyl group (H(9*B*)···O(15) 2.53 Å).

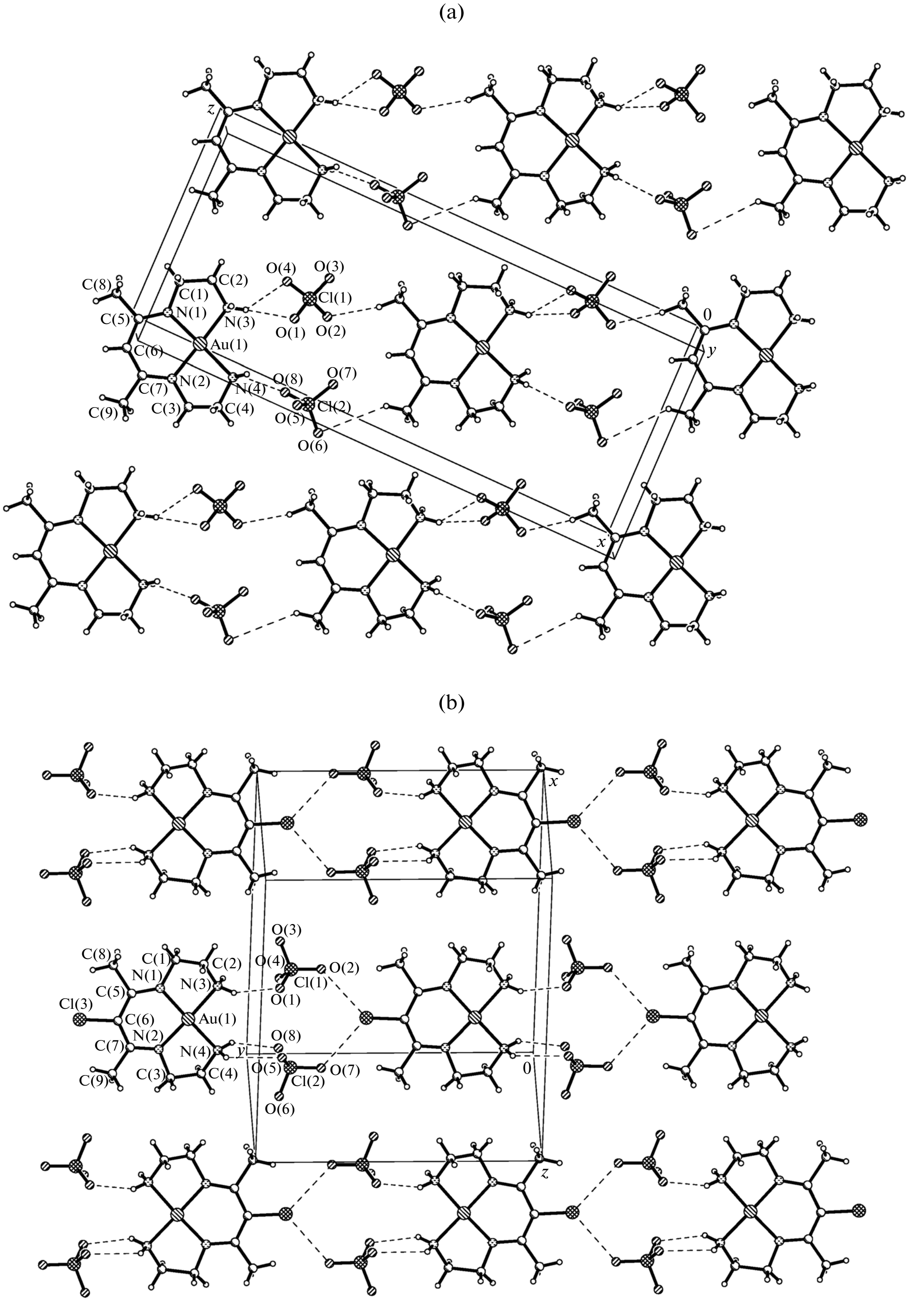

Fig. 1. View of the crystal structures on the plane (a) *xz* for **II**, (b) *xy* for **IV**, and (c) *xz* for **V**. Hydrogen bonds and contacts are shown by dash.

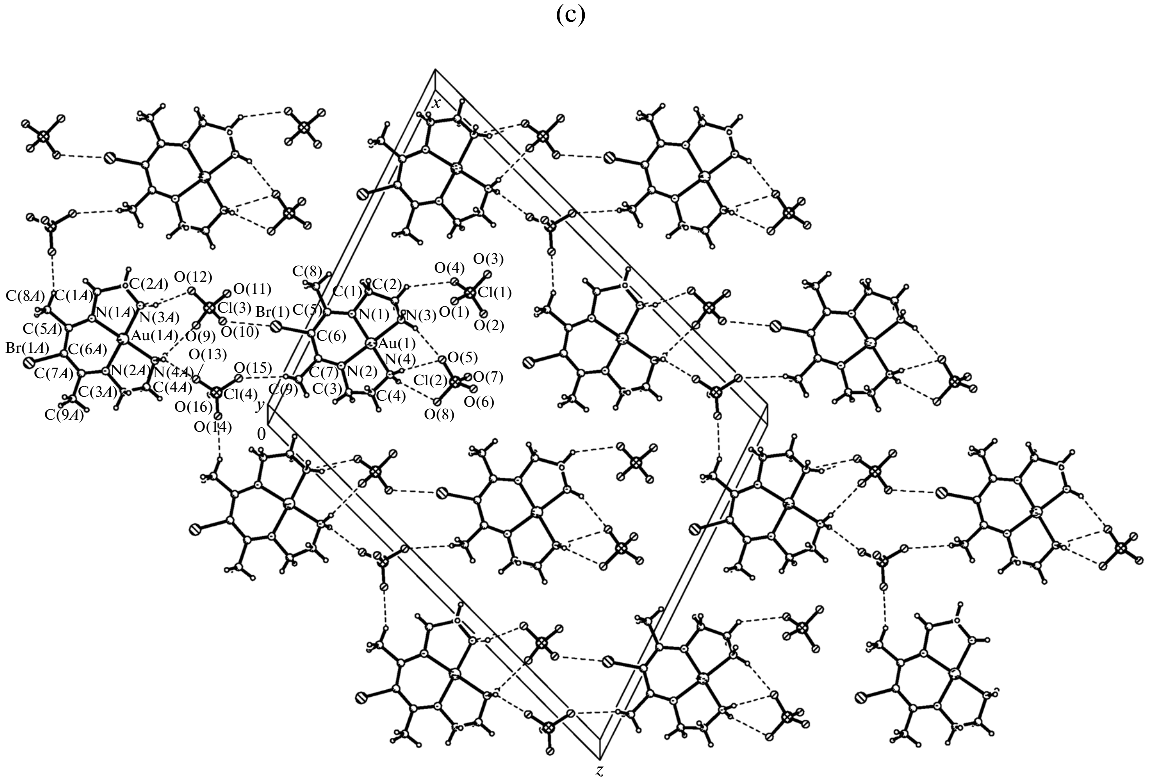

Fig. 1. (Contd.)

In compounds **II** and **IV**, the ribbons are linked by (N)H bonds from the side of the "tail" of the cation. In compound **V**, the methylene group of the ethylenediamine five-membered ring also participates in pseudoribbon formation. The deviations from the ribbon plane in complexes **I–IV** range from 0.02 to 0.22 Å, while in **V** they are 0.27 Å (Δ were calculated taking into account the atoms of the coordination AuN_4 nodes and central atoms of the anions). Unlike ribbons in complexes **I–IV**, the central gold atoms of the cations of the pseudoribbon in bromine complex **V** do not rigidly lie on the straight line: the Au(1)Au(1*A*)Au(1)' angle is 173.2°. The Au···Au spacing in the ribbon (pseudoribbon) increases when the H atom is replaced by Cl and Br (12.459(3) (**II**); 13.221(2) (**IV**); 13.204(3), 13.402(2) (**V**) Å), and the elongation of the distance correlates with the difference in van der Waals of hydrogen, chlorine, and bromine atoms ($r_H = 1.2$, $r_{Cl} = 1.8$, and $r_{Br} = 1.9$ Å [18]). The distance between the ribbons (pseudoribbons) in complexes **I–V** is 7.913–9.274 Å. Note that in bromine-substituted **V**, unlike unsubstituted **I–III** and chlorine-substituted **IV**, the pseudoribbons are linked to each other (in the direction of the *z* axis) by the C(8*A*)–H(8*AA*)···O(14) bond formed by the bridging $Cl(4)O_4^-$ anion.

The cation–anion ribbons (pseudoribbons) of complexes **IV** and **V** bound by symmetry elements in the short direction form the 2D layers, whose topological pattern is similar to that revealed in the structures of unsaturated complexes [14] and is characterized by the following common structural units.[2]

(1) Cations of all studied gold(III) iminatoamine complexes form 1D doubled cation–cation stacks along the short axes. Bonding in the stacks occurs due to C–H···π interactions [2, 8–12] of the hydrogen atoms of the terminal methyl groups of the cation with the atoms of the delocalized six-membered rings of the higher- and lower-lying cations (Table 3) to form two C–H···π chains.[3] In addition, in complex V the cations of the stacks are joined in pairs by the Au(1*A*)···Br(1) contacts and C(8*A*)–H(8*AC*)···Au(1) bonds to form closed cation–cation rings (Fig. 2a).

(2) Cavities between the stacks contain four infinite chains of the anions that form 1D columns of hydrogen bonds and contacts along the short axis of the crystalline lattice with the arranged outside amine "tails," methylene groups, and central gold atoms (Fig. 2a). The columns are composed of closed cation–anion rings of two types: "one cation–one anion" and "two

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[2] Since the topological pattern of packings of complexes **II**, **IV**, and **V** is similar, the 2D layer only for complex **V** is shown in Fig. 2a.

[3] The C–H···π chains for unsubstituted complexes **I–III** were considered in detail [14].

Table 3. Geometric parameters of hydrogen bonds and contacts in the structures of compounds II, IV, and V

D–H···A	Distance, Å			Angle DHA, deg	Symmetry transform for A
	D···A	H···A	D–H		
II [14]					
N–H···O					
N(3)–H(3*A*)···O(1)	3.08(2)	2.44	0.90	128	*x*, *y*, *z*
N(3)–H(3*A*)···O(1)	3.10(2)	2.53	0.90	121	1/2 – *x*, *y* – 1/2, 1/2 – *z*
N(3)–H(3*A*)···O(4)	2.97(2)	2.25	0.90	137	1/2 – *x*, *y* – 1/2, 1/2 – *z*
N(3)–H(3*B*)···O(7)	3.33(2)	2.58	0.90	141	*x*, *y*, *z*
N(3)–H(3*B*)···O(2)	2.99(2)	2.33	0.90	131	*x*, –1 + *y*, *z*
N(4)–H(4*A*)···O(4)	2.93(2)	2.08	0.90	156	*x*, –1 + *y*, *z*
N(4)–H(4*B*)···O(5)	3.05(2)	2.28	0.90	144	1/2 – *x*, *y* + 1/2, 1/2 – *z*
N(4)–H(4*B*)···O(3)	3.05(2)	2.44	0.90	125	*x*, *y*, *z*
C–H···O					
C(3)–H(3*A*)···O(5)	3.33(2)	2.54	0.97	139	1 + *x*, *y*, *z*
C(3)–H(3*B*)···O(3)	3.25(2)	2.59	0.97	126	*x*, *y*, *z*
C(8)–H(8*B*)···O(2)	3.28(2)	2.34	0.96	167	1 – *x*, 1 – *y*, 1 – *z*
C(9)–H(9*B*)···O(7)	3.46(2)	2.59	0.96	151	1 – *x*, –*y*, 1 – *z*
C–H···π					
C(8)–H(8*A*)···C(6)	3.63(2)	2.91	0.96	133	1 – *x*, 1 – *y*, 1 – *z*
C(8)–H(8*A*)···C(7)	3.71(2)	2.81	0.96	157	1 – *x*, 1 – *y*, 1 – *z*
C(8)–H(8*C*)···C(6)	3.72(2)	2.98	0.96	135	1 – *x*, –*y*, 1 – *z*
C(8)–H(8*C*)···C(7)	3.77(2)	2.85	0.96	160	1 – *x*, –*y*, 1 – *z*
C(8)–H(8*C*)···N(2)	3.77(2)	2.93	0.96	147	1 – *x*, –*y*, 1 – *z*
C(8)–H(8*C*)···L(1)*	3.49(1)	2.80	0.96	130	1 – *x*, –*y*, 1 – *z*
Contacts					
Au(1)···O(1)	3.41(1)				*x*, *y*, *z*
Au(1)···O(3)	3.22(1)				*x*, *y*, *z*
Au(1)···O(2)	3.17(1)				*x*, *y* – 1, *z*
IV					
N–H···O					
N(3)–H(3*A*)···O(5)	2.971(10)	2.36	0.90	125	*x* – 1/2, 3/2 – *y*, –1/2 + *z*
N(3)–H(3*A*)···O(1)	3.049(10)	2.29	0.90	142	*x*, 1 – *y*, –1/2 + *z*
N(3)–H(3*B*)···O(1)	3.106(10)	2.28	0.90	153	*x*, 1 + *y*, *z*
N(3)–H(3*B*)···O(4)	3.054(9)	2.47	0.90	123	*x*, 1 – *y*, 1/2 + *z*
N(4)–H(4*A*)···O(4)	2.976(8)	2.35	0.90	127	*x*, 1 – *y*, 1/2 + *z*
N(4)–H(4*A*)···O(8)	3.083(9)	2.37	0.90	136	*x* – 1/2, 3/2 – *y*, 1/2 + *z*
N(4)–H(4*A*)···O(5)	3.103(10)	2.58	0.90	118	*x* – 1/2, 1/2 + *y*, *z*
N(4)–H(4*B*)···O(5)	3.011(9)	2.40	0.90	125	*x* – 1/2, 3/2 – *y*, –1/2 + *z*
N(4)–H(4*B*)···O(8)	3.124(10)	2.33	0.90	147	*x* – 1/2, 1/2 + *y*, *z*
C–H···O					
C(4)–H(4*A*)···O(6)	3.362(9)	2.56	0.97	140	*x* – 1/2, 3/2 – *y*, –1/2 + *z*
C(9)–H(9*C*)···O(3)	3.373(9)	2.50	0.97	151	*x* – 1/2, 1/2 – *y*, 1/2 + *z*
C–H···π					
C(8)–H(8*A*)···C(5)	3.536(9)	2.85	0.96	129	*x*, 1 – *y*, –1/2 + *z*
C(8)–H(8*A*)···C(6)	3.451(11)	2.90	0.96	117	*x*, 1 – *y*, –1/2 + *z*
C(9)–H(9*A*)···C(6)	3.494(12)	3.16	0.96	102	*x*, 1 – *y*, 1/2 + *z*
C(9)–H(9*A*)···C(7)	3.647(10)	3.16	0.96	114	*x*, 1 – *y*, 1/2 + *z*
Contacts					
Au(1)···O(2)	3.68(1)				*x*, 1 – *y*, 1/2 + *z*
Au(1)···O(4)	3.149(5)				*x*, 1 – *y*, 1/2 + *z*
Au(1)···O(5)	3.144(6)				*x* – 1/2, 3/2 – *y*, –1/2 + *z*
Cl(3)···O(2)	3.174(9)				*x*, *y*, *z*
Cl(3)···O(7)	3.181(8)				*x* – 1/2, –1/2 + *y*, *z*

Table 3. (Contd.)

D–H···A	Distance, Å			Angle DHA, deg	Symmetry transform for A
	D···A	H···A	D–H		
V					
K(1)					
N–H···O					
N(3)–H(3*A*)···O(5)	3.063(4)	2.28	0.90	146	*x*, 3/2 – *y*, 1/2 + *z*
N(3)–H(3*A*)···O(1)	2.988(4)	2.46	0.90	117	*x*, 5/2 – *y*, 1/2 + *z*
N(3)–H(3*B*)···O(7)	2.945(5)	2.25	0.90	134	1 – *x*, 1 – *y*, 1 – *z*
N(4)-H(4*A*)···O(4)	2.882(4)	2.03	0.90	157	*x*, 3/2 – *y*, 1/2 + *z*
N(4)-H(4*A*)···O(5)	2.890(3)	2.40	0.90	114	*x*, 3/2 – *y*, 1/2 + *z*
N(4)-H(4*B*)···O(8)	3.023(4)	2.35	0.90	132	*x*, 3/2 – *y*, 1/2 + *z*
N(4)-H(4*B*)···O(3)	3.156(4)	2.55	0.90	125	*x*, 5/2 – *y*, 1/2 + *z*
C–H···O					
C(1)–H(1*B*)···O(7)	3.058(5)	2.35	0.97	129	1 – *x*, 1 – *y*, 1 – *z*
C(2)–H(2*A*)···O(4)	3.331(5)	2.56	0.97	136	1 – *x*, 2 – *y*, 1 – *z*
C(2)–H(2*B*)···O(5)	3.213(4)	2.52	0.97	128	1 – *x*, 2 – *y*, 1 – *z*
C(2)–H(2*B*)···O(1)	3.209(6)	2.58	0.97	122	*x*, 5/2 – *y*, 1/2 + *z*
C(9)–H(9*B*)···O(15)	3.326(6)	2.53	0.97	140	*x*, 3/2 – *y*, 1/2 + *z*
C–H···π					
C(8)–H(8*B*)···C(6*A*)	3.756(5)	2.97	0.96	140	–*x*, 2 – *y*, –*z*
C(8)–H(8*B*)···C(7*A*)	3.940(5)	3.00	0.96	165	–*x*, 2 – *y*, –*z*
C(8)–H(8*C*)···C(6*A*)	3.678(5)	2.91	0.96	138	–*x*, 1 – *y*, –*z*
C(8)–H(8*C*)···C(7*A*)	3.894(5)	2.97	0.96	161	–*x*, 1 – *y*, –*z*
Contacts					
Au(1)···O(1)	3.364(3)				*x*, 5/2 – *y*, 1/2 + *z*
Au(1)···O(3)	3.287(3)				*x*, 5/2 – *y*, 1/2 + *z*
Au(1)···O(2)	3.188(3)				*x*, 3/2 – *y*, 1/2 + *z*
Br(1)···Au(1*A*)	3.724(1)				–*x*, 1 – *y*, –*z*
Br(1)···O(10)	2.883(1)				*x*, *y*, *z*
K(1*A*)					
N–H···O					
N(3*A*)–H(3*AA*)···O(12)	2.893(3)	2.06	0.90	153	*x*, 3/2 – *y*, –1/2 + *z*
N(3*A*)–H(3*AB*)···O(15)	3.078(4)	2.28	0.90	147	–*x*, –1/2 + *y*, –1/2 – *z*
N(3*A*)–H(3*AB*)···O(10)	3.111(4)	2.52	0.90	123	–*x*, 1 – *y*, –*z*
N(4*A*)–H(4*AA*)···O(10)	3.075(4)	2.51	0.90	122	–*x*, 1 – *y*, –*z*
N(4*A*)-H(4*AA*)···O(12)	3.058(4)	2.33	0.90	138	–*x*, 1 – *y*, –*z*
N(4*A*)-H(4*AA*)···O(9)	3.139(4)	2.38	0.90	142	*x*, 3/2 – *y*, –1/2 + *z*
N(4*A*)-H(4*AB*)···O(9)	3.229(4)	2.51	0.90	137	–*x*, 2 – *y*, –*z*
N(4*A*)-H(4*AB*)···O(11)	3.098(4)	2.51	0.90	123	–*x*, 2 – *y*, –*z*
N(4*A*)-H(4*AB*)···O(13)	3.050(4)	2.31	0.90	139	*x*, *y*, *z*
C–H···O					
C(3*A*)–H(3*AB*)···O(11)	3.236(5)	2.57	0.97	126	–*x*, 2 – *y*, –*z*
C(8*A*)–H(8*AA*)···O(14)	3.208(8)	2.31	0.97	155	–*x*, 3/2 – *y*, –1/2 + *z*
C(9*A*)–H(9*AC*)···O(6)	3.249(5)	2.46	0.97	139	–*x*, 2 – *y*, –*z*
C–H···Au					
C(8*A*)–H(8*AC*)···Au(1)	4.103(4)	3.17	0.96	166	–*x*, 2 – *y*, –*z*
C–H···π					
C(8*A*)–H(8*AB*)···C(6)	3.754(5)	3.11	0.96	126	–*x*, 2 – *y*, –*z*
C(8*A*)–H(8*AB*)···C(7)	3.777(5)	3.12	0.96	127	–*x*, 2 – *y*, –*z*
C(8*A*)–H(8*AC*)···N(2)	3.677(5)	2.94	0.96	135	–*x*, 1 – *y*, –*z*
C(8*A*)–H(8*AC*)···C(5)	3.931(5)	3.18	0.96	137	–*x*, 1 – *y*, –*z*
C(8*A*)–H(8*AC*)···C(6)	3.643(5)	3.03	0.96	123	–*x*, 1 – *y*, –*z*
C(8*A*)–H(8*AC*)···C(7)	3.656(5)	3.05	0.96	122	–*x*, 1 – *y*, –*z*
Contacts					
Au(1*A*)···O(9)	3.644(3)				–*x*, 2 – *y*, –*z*
Au(1*A*)···O(11)	3.238(3)				–*x*, 2 – *y*, –*z*
Au(1*A*)···O(10)	3.176(3)				–*x*, 1 – *y*, –*z*
Au(1*A*)···Br(1)	3.724(1)				–*x*, 1 – *y*, –*z*

* L(1) is the middle point of the six-membered ring in the complex cation.

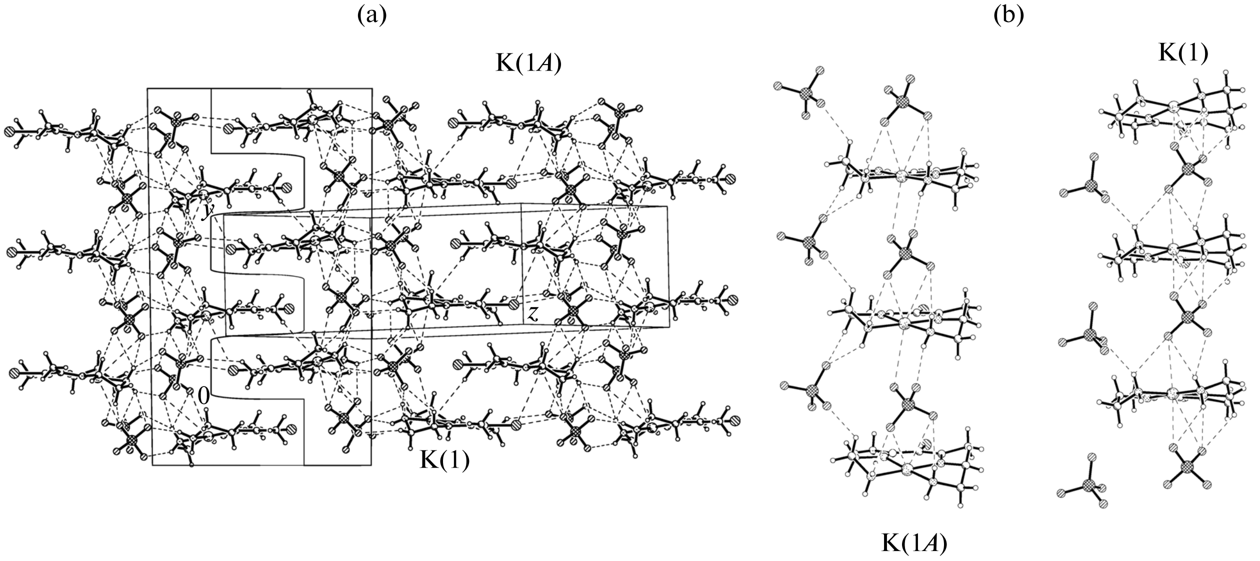

Fig. 2. (a) The 2D layer in the structure of complex **V** in the plane (1 0 $\bar{1}$) and (b) fragments of the layer illustrating the bonds and contacts between the cations K(1) and K(1*A*) translationally identical in the short axis direction.

cations–two anions." The predominant part of hydrogen bonds in the columns is formed by the hydrogen atoms of the amino groups.

(3) Each cation of the doubled stack in the region of five-membered rings forms several hydrogen bonds and Au···A contacts with one of the higher- and lower-lying anions. For example, in hexafluorophosphate complex **III**, the cation forms five hydrogen bonds and contacts with the higher-lying anion $P(2)F_6^-$, and six hydrogen bonds and contacts with the lower-lying anion $P(1)F_6^-$ [14]. Figure 2b shows the isolated fragments of the 2D layer for complex **V** illustrating the bonds and contacts between the cations and anions translationally identical in the short axis direction. It is seen that each cation of the complex (K(1) and K(1*A*)) also forms more hydrogen bonds and contacts with one of the anions. In all studied iminatoamine complexes **I–V**, the quadrangles AuNHA formed by hydrogen bonds N–H···A and contacts Au···A (A = I, O, F) are nearly planar: Δ = 0.04; 0.08 (**I**), 0.04–0.11 (**II**), 0.08–0.16 (**III**), 0.07–0.10 (**IV**), and 0.08–0.15 Å (**V**).

(4) The translationally identical cations of the doubled stacks of complexes **I–V** from the "tail" side are penetrated by cation–anion chains formed due to the hydrogen bonds of both hydrogen atoms of the NH_2 groups (and CH_2 groups in **I** [14]) or contacts of the central gold atom with the same higher- and lower-lying anions. Each chain consists of two independent hydrogen bonds (or Au···A contacts). The N atoms of the amino groups, the C atoms of the methylene groups, or the Au atoms of the cation and the I, Cl, and F atoms of the anions are bridging atoms in the chains. In complex **V**, the chains of hydrogen bonds and contacts form both independent cations K(1) and K(1*A*) (Fig. 2b). Note that the A···H–N–H···A' fragments of the chains are nearly planar in all iminatoamine complexes: in unsubstituted **I–III** Δ is 0.06–0.19 Å, and in halogen-substituted **IV** and **V** Δ is 0.11–0.15 Å.

(5) The stacks and columns are joined into 2D layers by cation–anion hydrogen bonds and contacts of the ribbons (pseudoribbons). The joining occurs due to hydrogen bonds C–H···A of the methyl groups in unsubstituted complexes **I–III** [14], due to contacts Cl(3)···O(7) and Cl(3)···O(2) in chlorine-substituted complex **IV**, and due to contacts Br(1)···O(12) and hydrogen bonds C(9)–H(9*B*)···O(15) in bromine-substituted complex **V** (Table 3).

The layers of complexes **I–V** are joined into a 3D lattice by nonclassical C–H···O bonds. In unsubstituted **I–III**, the layers are bonded through both methyl and methylene groups [14], whereas in **IV** and **V** these are only methyl groups: C(9)–H(9*C*)···O(3) (**IV**); C(8*A*)–H(8*AA*)···O(14), C(9*A*)–H(9*AC*)···O(6)) (**V**) (Fig. 3). Note that only one of two independent anions ($I(2)^-$ (**I**), $Cl(2)O_4^-$ (**II**), $P(1)F_6^-$ (**III**), $Cl(1)O_4^-$ (**IV**)) is involved in the formation of 3D frameworks in complexes **I–IV**, whereas two of four independent anions ($Cl(2)O_4^-$ and $Cl(4)O_4^-$) participate in 3D framework formation in complex **V**.

When characterizing the local geometry of hydrogen bonds in the studied gold(III) iminatoamine complexes, we should first mention the ability of the amino groups to form multicentered, chelate, and chain hydrogen bonds. In all cases, a tendency for forming planar structural units is observed. The bifurcated hydrogen bonds N–H···A,A' are planar in all complexes (Δ = 0.003–0.09 Å). For the trifurcated hydro-

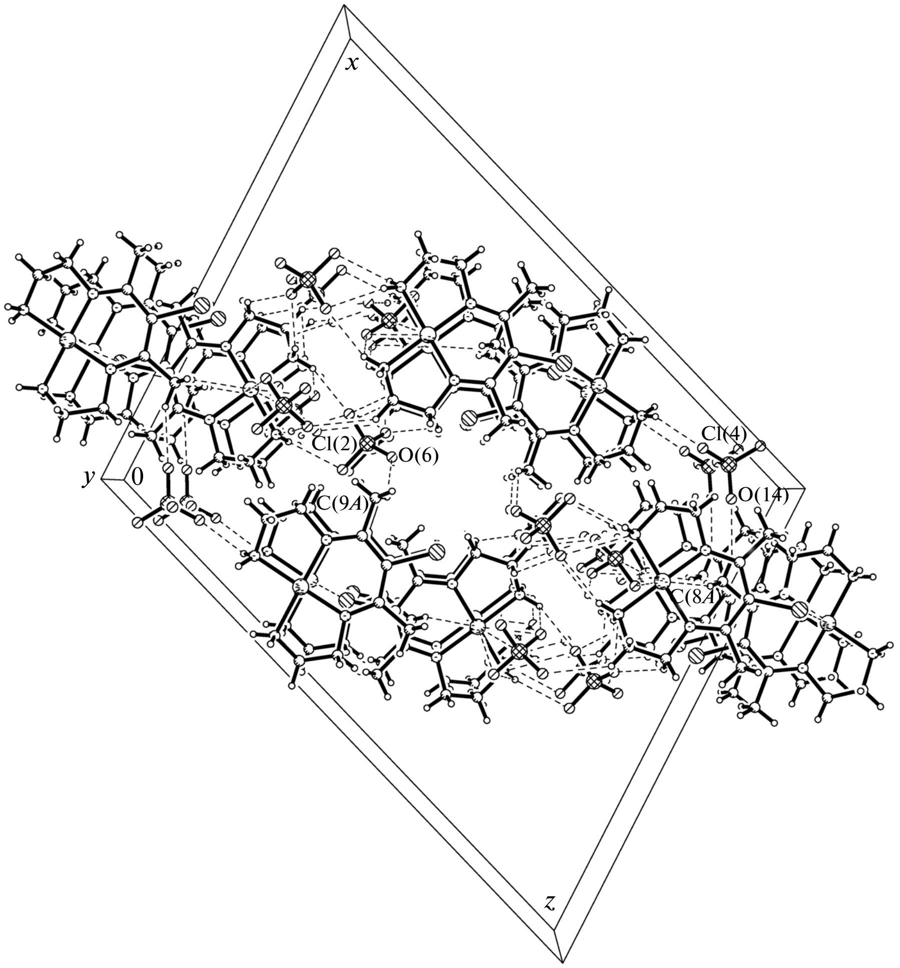

Fig. 3. Packing fragment of ions along the direction [010] for structure **V**.

gen bonds N–H···A,A',A'', two of three N–H···A bonds lie in one plane (Δ = 0.02–0.09 Å). In the chelate hydrogen bond of the N–H(H)···**I** type that is observed in complex **I** [14], the acceptor atom is localized in the amino group plane (Δ = 0.09 Å). For chelating hydrogen bonds N–H···O(O')Cl and N–H···F(F')P in the complexes with polyatomic anions ClO_4^- and PF_6^-, on the contrary, the hydrogen atom lies in the plane of the acceptor groups; that is, quadrangles HOO'Cl (**II**, **V**) (Δ = 0.06–0.10 Å) and HFF'P (**III**) (Δ = 0.17; 0.21 Å) are planar.

Nearly all negative out-of-sphere atoms (6 oxygen atoms in **II**, all 12 fluorine atoms in **III**, all 8 oxygen atoms in **IV**, and 15 oxygen atoms of 16 atoms in **V**) are involved in hydrogen bonds and contacts in the complexes with polyatomic anions, and each atom forms from one to four hydrogen bonds and contacts.

To summarize, the 3D supramolecular architecture of the crystalline lattice of the iminatoamine complexes determined and stabilized by a vast lattice of intermolecular interactions (hydrogen bonds and contacts Au···A) has a series of typical characteristic features and is independent of the type of the anion [14] and substitution in the delocalized ring. The halogenation of the cation affects only the number of cations and anions in the closed rings that form the 2D layers. The local geometry of hydrogen bonds also remains unchanged.

The method of crystal packing organization of the gold(III) iminatoamine complexes that takes place in the structure can be attributed to both the ability of ions of the complex to act as hydrogen bond donors or acceptors and the composition and structure of the metallocyclic cation.

The cations of the gold(III) iminatoamine complexes studied in this work and in [14] have 18 hydrogen atoms in the composition of several functional groups, being potential donors of medium (NH_2) or weak (CH_3, CH_2) hydrogen bonds [19, 20]. All hydrogen atoms of these groups are at the periphery of the cation and are accessible for hydrogen bond formation. The acceptor properties in the system are manifested by the anions (strong acceptors of hydrogen bonds [21]) and the central gold atoms and delocalized rings of cations (weak acceptors of hydrogen bonds [7, 8]).

The determining role in the topological pattern of the packing of the complexes belongs to the structure of the cation, namely, its planarity provided by a combination of the planar AuN_4 coordination node with the planar delocalized AuNCCCN ring along with the presence of two coordinated amino groups in the *cis*-position of the AuN_4 square and two methyl groups in the α-position of the six-membered delocalized ring. It is the planar structure of the cation that warrants spatial accessibility of both delocalized iminate rings (for their participation as acceptors in the formation of the nonclassical C–H···π bonds forming the doubled stacks) and the central Au atom (for the formation of translationally identical along the short axis and supplementing its coordination A···Au···A' contacts with the higher- and lower-lying anions and of the C–H···Au bonds (in **I** and **V**) between the pairs of cations in the doubled stacks).

The arrangement of the amino groups in the *cis*-position of the AuN_4 square along with the ability of the hydrogen atoms and anions to form multicentered bonds provide a potent possibility for the formation of a complex of hydrogen bonds forming columns of (N)H bonds along the short axis. The NH vectors of the amino groups containing the nitrogen atoms in the sp^3 state are oriented up and down from the cation plane, thus providing prerequisites for the formation of chains of hydrogen bonds with the higher- and lower-lying anions.

The methyl groups of the cation lie in the plane of the six-membered ring and are arranged symmetrically relative to its central β-carbon atom. They are not rigid, have the free degree of rotation around the C–C axis, and are oriented in the structures of the iminatoamine complexes in such a way that two of six hydrogen atoms of the methyl groups are involved in the formation of the C–H···π chains linking the cations into the doubled stacks in the short axis direction. Two hydrogen atoms (in **I–III**) or one (in **V**) hydrogen atom form hydrogen bonds C–H···A of the ribbons (pseudoribbons) and one (in **I**, **III**, **IV**) or two (in **V**) hydrogen atoms perform the function of binding the layers into a three-dimensional framework. Note that the "activity" of the methyl groups of the complexes is substantially higher than that of the methylene groups: four methylene groups form from one to four hydrogen bonds in structures **I–V**, and two methyl groups form from three to six hydrogen bonds.

The covalently bonded halogen atoms in the β-position of the six-membered ring manifest no acceptor properties in the structures of the substituted complexes but functionally play a special role participating due to contacts Hal···O in the formation of 2D layers and due to contacts Br···Au in the formation of cation–cation rings in the layers (in **V**).

Since the substitution of hydrogen atoms for halogen in the six-membered ring of the cation does not substantially change the cation structure (the bond lengths and bond angles remain unchanged), its structure forming role remains almost unchanged. The changes concern only hydrogen bonds C–H···A. In the unsubstituted complexes, they fasten together the columns and stacks into a 2D layer. In Br-substituted **V**, they participate in the formation of the layer along with contacts O···Hal, and contacts Cl···O perform this function in Cl-substituted **IV**.

To conclude, the general empirical Etter's rules [22] are appropriate for the gold(III) iminatoamine complexes: all efficient donor and acceptor groups are involved in hydrogen bonds to form, first of all, bonds between each other. Weaker donors can form hydrogen bonds only in the presence of excessive acceptors that were not involved in bonding after the formation of hydrogen bonds with efficient donors) acceptors. In the studied iminatoamine complexes (both unsubstituted with different anions and halogen-substituted), the amino groups manifest themselves as active donors and the anions are active acceptors. Each hydrogen atom of the amino groups forms a hydrogen bond (two-, three-, or four-centered) only with strong acceptors (anions) to form one-dimensional columns. The hydrogen atoms of the methyl groups (weak donors) form hydrogen bonds with both strong (anions) and weak (the central Au atom and delocalized ring of the cation) acceptors. The bonds with the weak acceptors form the binding cations into stacks vertical 1D chains (C–H···π) or cation–cation rings (C–H···Au), whereas the bonds with the strong acceptors form the 3D structure; that is, the strong donor interact with the strong acceptors only and the strong acceptor tends to bind both strong and weak donors by hydrogen bonds.

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