ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 3, pp. 257–270. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © V.A. Afanas'eva, L.A. Glinskaya, I.V. Korol'kov, 2013, published in Koordinatsionnaya Khimiya, 2013, Vol. 39, No. 3, pp. 160–173.

Intermolecular Interactions in the Acyclic Tetraazagold(III) Metal Complexes

V. A. Afanas'eva*, L. A. Glinskaya, and I. V. Korol'kov

Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences,
pr. akademika Lavrent'eva 3, Novosibirsk, 630090 Russia
**e-mail: l311@niic.nsc.ru*

Received July 27, 2012

Abstract—The packings of the crystal structures of the gold(III) iodide, perchlorate, and hexafluorophosphate complexes with the iminate–amine ligand, $[Au(C_9H_{19}N_4)]Y_2$ (Y = I (**I**), ClO_4 (**II**), and PF_6 (**III**)), are studied in comparison. The packings of structures **I**–**III** are similar. They are determined and stabilized by a vast network of intermolecular interactions (hydrogen bonds N–H···A, C–H···A, C–H···Au, and C–H···π and short contacts Au···A (A = I, O, F)). Structures **I**–**III** are characterized by cation-cationic and cation-anionic infinite chains and closed rings formed by classical and nonclassical hydrogen bonds and contacts. The structures include multicentered hydrogen bonds. The replacement of the anion does not basically change the packing structures.

DOI: 10.1134/S1070328413030019

At present many efforts are devoted to the recognition of intermolecular interactions (hydrogen bonds, short contacts, and others) and elucidation of their role in crystal structure stabilization because of the appearance of supramolecular chemistry and crystal engineering. The understanding of factors responsible for bonding in inorganic and organometallic solids and the revealing of the regularities of their architecture and, in particular, hydrogen bond geometry in crystals, seem to be important and urgent. In recent decades the main section in the investigation of hydrogen bonds (being the most important of all directed intermolecular interactions) are weak and nonclassical types of hydrogen bonds that are especially significant in structural chemistry and biology [1, 2]. The influence of donors and acceptors of hydrogen bonds on the crystal packing was studied [3]. It was shown [4–6] that counterions can play a substantial role in the formation of the metal complex structures, determining both the coordination mode of the ligand and geometry of the central atom.

The gold(III) complexes have a series of specific features that make them promising for use, for example, in medicine [7]. We synthesized and studied a series of the gold(III) tetraazametallocyclic complexes to the central atom of which the nitrogen atoms in different electronic states are coordinated (amine $>NH_2$, iminate $>N\overset{---}{-}$, imine >N=) [8]. 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 associated with their packing; however, no systematic comparative analysis was performed for the mutual arrangement of ions in the complexes, depending on the type of the cation (macrocyclic or acyclic), modification of the ligand (protonated or substituted), or the type of the anion. Intermolecular interactions in the crystal structure of the gold(III) iodide acyclic complex, $[Au(C_9H_{19}N_4)]I_2$, $[AuL]I_2$ (**I**), whose ligand contains the iminate and amine nitrogen atoms, were examined [9]. It is shown that structure **I** is determined and stabilized by weak N–H···I, C–H···I, C–H···Au hydrogen bonds and short Au···I contacts forming infinite chains and closed polyatomic rings. The structural data for the $[AuL](ClO_4)_2$ (**II**) perchlorate complex are presented [10]; however, there is no detailed description of the packing.

In this work, the synthesis of the hexafluorophosphate iminate–amine complex with the same cation $[AuL](PF_6)_2$ (**III**) is described and the secondary interactions in the crystal structures of iodide complex **I** [9] and complexes **II** and **III** with polyatomic anions are compared in detail. The study was carried out to reveal the role of cations and anions in the formation of the structures of the heterocyclic tetraazagold(III) metal complexes and the regularities of the mutual arrangement and geometry of hydrogen bonds and short contacts in the structures.

EXPERIMENTAL

The following reagents were used: potassium hexafluorophosphate (high-purity grade), ethanol (rectificate), and diethyl ether (medicinal). Acetylacetone (analytical grade) was distilled. Complex

Table 1. Crystallographic characteristics and experimental and structure refinement details for the structures of compounds **I–III**

Parameter	Value		
Molecular formula	$C_9H_{19}AuI_2N_4$ [9]	$C_9H_{19}AuCl_2N_4O_8$	$C_9H_{19}AuF_{12}N_4P_2$
FW	634.05	579.15	670.19
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
a, Å	6.7945(2)	9.9807(2)	8.7368(3)
b, Å	9.6930(3)	7.0670(2)	12.7700(4)
c, Å	12.1961(3)	23.1451(6)	16.3423(5)
α, deg	68.781(1)		
β, deg	89.780(1)	91.925(1)	97.015(1)
γ, deg	84.979(1)		
V, Å^3	745.56(4)	1631.59(7)	1809.64(10)
Z; ρ_{calcd}, g/cm^3	2, 2.824	4, 2.358	4, 2.460
μ, mm^{-1}	13.990	9.392	8.429
Crystal sizes, mm	0.21 × 0.2 × 0.17	0.17 × 0.15 × 0.09	0.12 × 0.18 × 0.13
Scan range, θ, deg	1.79–30.53	1.76–25.08	2.51–30.65
Number of measured reflections	15380	10960	21500
Number of independent reflections	4527	2887	5538
R_{int}	0.0277	0.0415	0.0391
Number of reflections with $I > 2\sigma(I)$	4527	2887	5538
Number of refined parameters	162	236	270
Goodness-of-fit on F^2	1.177	1.529	0.979
R factor, $I > 2\sigma(I)$	$R_1 = 0.0209$ $wR_2 = 0.0480$	$R_1 = 0.0416$ $wR_2 = 0.1108$	$R_1 = 0.0277$ $wR_2 = 0.04590$
R factor (on all I_{hkl})	$R_1 = 0.0225$ $wR_2 = 0.0574$	$R_1 = 0.0458$ $wR_2 = 0.1169$	$R_1 = 0.0431$ $wR_2 = 0.0493$
Residual electron density (max/min) e/Å^3	2.607/–2.902	2.518/–1.325	1.665/–1.111

$Au(En)_2Cl_3$ necessary for the synthesis of the acyclic cation was obtained according to a described procedure [11]. *N,N*-Bis(2-aminoethyl)-2,4-pentane diiminatogold(III) bishexafluorophosphate $[Au(C_9H_{19}N_4)](PF_6)_2$ was synthesized according to a published procedure [12] using KPF_6 for the precipitation of the product.

Synthesis. Acetylacetone (0.31 mL) was added dropwise to a solution of $Au(En)_2Cl_3$ (0.5 g) in water (20 mL), maintaining pH 8.5. The solution was stirred at ambient temperature for 7 min and filtered off. A brick-brown precipitate was formed upon the addition of an excess of solid KPF_6 (1.35 g) to the solution and dissolved on the filter in water (17 mL) and reprecipitated by adding KPF_6 (1.0 g) to the filtrate. A fluffy brick-red precipitate was filtered off, washed with cool ethanol (three times, 3–5 mL each) and ether, and dried. The yield was 0.19 g (24%).

For $C_9H_{19}N_4F_{12}P_2Au$
anal. calcd. (%): C, 16.15; H, 2.71; N, 8.37.
Found (%): C, 16.1; H, 3.0; N, 8.3.

Elemental analysis was carried out at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences). The compound is stable in air at ambient temperature.

X-ray diffraction analysis. Single crystals of compound **III** were grown by keeping an aqueous solution of the precipitate (15.5 mg) at 5°C for several days. Unit cell parameters and reflection intensities of compounds **II** and **III** 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 of X-ray diffraction experiment and structure refinement are given in Table 1. The structures were solved by a direct method

---

[1] The X-ray diffraction data for compound **II** obtained at ambient temperature are published [10]. The crystallographic characteristics almost coincide with those obtained in the present work; however, one of the perchlorate groups is disordered.

and refined by least squares for F^2 in the anisotropic (for non-hydrogen atoms) approximation using the SHELXL-97 program package [13]. Positions of hydrogen atoms were localized from the electron density difference synthesis and included into refinement in the isotropic approximation together with non-hydrogen atoms. Selected interatomic distances and bond angles are listed in Table 2. The full tables of atomic coordinates, bond lengths, and bond angles were deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 888053 (**II**) and 825617 (**III**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/data_request/cif) and are available from the authors.

RESULTS AND DISCUSSION

The $[Au(C_9H_{19}N_4)]^{2+}$ cation in complexes **I–III** includes only hydrogens as peripheral atoms in the composition of several functional groups, each of which is a potential donor of hydrogen bonds (medium or weak) [14, 15]. Hydrogen bonds can be enhanced by the interaction with strong acceptors or when the donor has a positive charge and the acceptor is negatively charged [16]. In particular, it is shown [17] that the fluorine atom in the hexafluorophosphate organometallic salts forms hydrogen bonds with a series of donors, and the D–H···F(P) interaction is enhanced by different charges of the cation and anion.

It is known that negatively charged anions, particularly, halide ions, are good proton acceptors [18]. The I^-, ClO_4^-, and PF_6^- , anions of studied complexes **I–III** bearing an electron density excess on the acceptor group and several lone electron pairs are capable of forming bonds and contacts simultaneously with more than one donor. Multicentered hydrogen bonds are especially observed for the formation of bonds between heavy halogens with the C–H groups, which is favored by steric factors (a large size of the halide ion and a relatively long H···Hal$^-$ distance) [18]. Perchlorate and hexafluorophosphate anions, which are most frequently used for the precipitation and crystallization of both organic and organometallic and inorganic cations, are also prone to multiple interactions binding the cations in crystals into one-, two-, or three-dimensional structures (for the perchlorate [4, 19, 20] and hexafluorophosphate [17, 21] salts). Thus, taking into account that all hydrogen-containing functional groups of the cation are potential donors of hydrogen bonds and potential proton acceptors are prone to the formation of multiple bonds, one can expect a branched network of hydrogen bonds in the structures of the complexes.

The crystal structures of compounds **I–III** are ionic. They consist of the $[Au(C_9H_{19}N_4)]^{2+}$ complex cations and crystallographically independent out-of-sphere anions Y(1)$^-$ and Y(2)$^-$.

Table 2. Selected bond lengths (d, Å) and bond angles (ω, deg) in the structures of compounds **I–III***

Bond	**I** [9]	**II**	**III**
	d, Å		
Au(1)–N(1)	1.976(3)	1.976(9)	1.976(3)
Au(1)–N(2)	1.986(3)	1.982(9)	1.980(3)
Au(1)–N(3)	2.048(3)	2.036(10)	2.052 (3)
Au(1)–N(4)	2.043(4)	2.046(10)	2.040(3)
N(1)–C(5)	1.331(5)	1.315(15)	1.339(4)
N(1)–C(1)	1.474(6)	1.476(15)	1.474(4)
N(2)–C(7)	1.317(5)	1.326(15)	1.329(4)
N(2)–C(3)	1.479(5)	1.473(14)	1.478(4)
N(3)–C(2)	1.430(8)	1.473(17)	1.485(4)
N(4)–C(4)	1.488(6)	1.484(17)	1.492(4)
C(1)–C(2)	1.387(9)	1.496(19)	1.518(5)
C(3)–C(4)	1.503(7)	1.512(18)	1.508(5)
C(5)–C(6)	1.401(6)	1.392(17)	1.395(5)
C(5)–C(8)	1.510(6)	1.498(16)	1.506(4)
C(6)–C(7)	1.401(6)	1.391(16)	1.401(5)
C(7)–C(9)	1.505(6)	1.507(16)	1.504(4)
Angle	ω, deg		
N(1)Au(1)N(2)	95.1(1)	95.1(4)	95.7(1)
N(1)Au(1)N(4)	177.9(1)	178.7(4)	178.1(1)
N(2)Au(1)N(4)	83.0(2)	83.7(4)	83.4(1)
N(1)Au(1)N(3)	83.8(1)	83.0(4)	83.6(1)
N(2)Au(1)N(3)	178.3(2)	178.9(4)	177.5(1)
N(4)Au(1)N(3)	98.1(2)	98.2(4)	97.4(1)
C(5)N(1)C(1)	123.1(4)	122.5(10)	122.8(3)
C(5)N(1)Au(1)	123.7(3)	123.5(8)	123.3(2)
C(1)N(1)Au(1)	113.1(3)	113.2(7)	113.1(2)
C(7)N(2)C(3)	123.2(4)	123.9(10)	123.0(3)
C(7)N(2)Au(1)	123.2(3)	123.2(8)	123.5(2)
C(3)N(2)Au(1)	113.1(3)	112.3(7)	113.0(2)
C(2)N(3)Au(1)	107.8(3)	107.4(8)	107.1(2)
C(4)N(4)Au(1)	105.8(3)	107.7(7)	107.9(2)
C(2)C(1)N(1)	110.9(4)	108.3(10)	107.8(3)
C(1)C(2)N(3)	119.8(6)	108.1(11)	107.9(3)
N(2)C(3)C(4)	108.1(3)	107.2(10)	107.7(3)
N(4)C(4)C(3)	107.5(4)	108.3(10)	107.7(3)
N(1)C(5)C(6)	124.0(4)	124.3(11)	124.0(3)
N(1)C(5)C(8)	117.9(4)	118.0(11)	118.1(3)
C(6)C(5)C(8)	118.1(4)	117.7(10)	118.0(3)
C(5)C(6)C(7)	128.6(4)	129.0(11)	129.4(3)
N(2)C(7)C(6)	124.6(4)	124.3(11)	124.0(3)
N(2)C(7)C(9)	118.1(4)	117.8(11)	118.0(3)
C(6)C(7)C(9)	117.2(4)	117.9(11)	117.9(3)

* For complex **II**, the Cl–O bond lengths and the OClO angles range from 1.393(11) to 1.447(10) Å and from 106(1)° to 112.9(10)°, respectively. For complex **III**, the P–F bond lengths and the FPF angles range from 1.583(2) to 1.609(2) Å and from 88.2(1)° to 90.7(1)°, respectively.

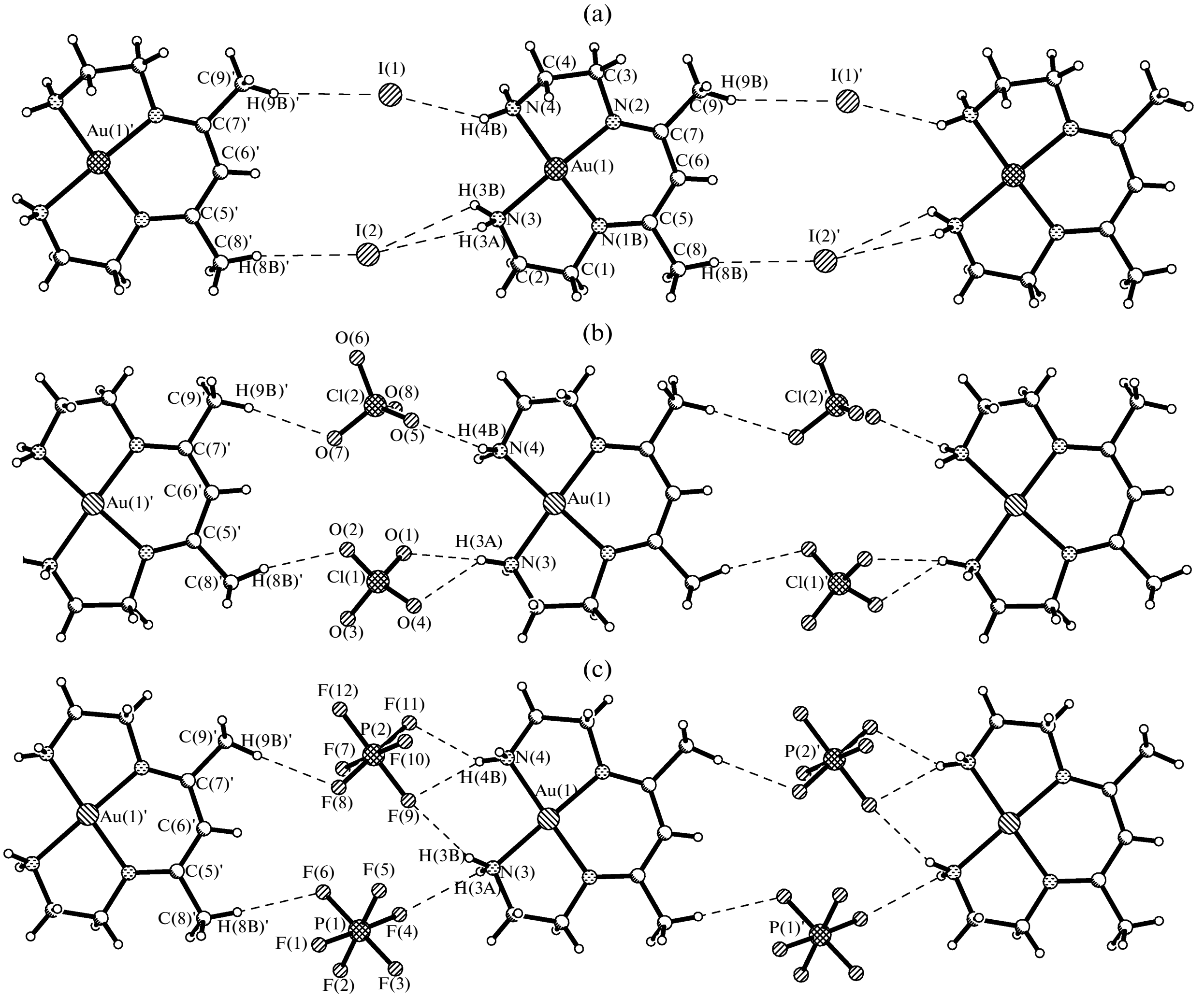

Fig. 1. Strips of the alternating cations and anions: (a) in complex **I** along the *z* axis, (b) in complex **II** along the *xz* diagonal, and (c) in complex **III** along the *y* axis. Hydrogen bonds are shown by dotted lines.

The acyclic complex cation $[Au(C_9H_{19}N_4)]^{2+}$ containing two five-membered rings and one six-membered ring (Fig. 1) is nearly planar (all non-hydrogen atoms deviate from the root-mean-square plane of atoms by 0.171(5) Å (**I**), 0.20(1) Å (**II**), 0.180(3) Å, (**III**). The coordination sphere of the gold atom includes four nitrogen atoms (Au–N 1.976(3)–2.052(3) Å) (Table 2). The both five-membered ethylenediamine rings have an envelope conformation: the C(2) atom deviates from the root-mean-square plane of atoms Au(1)N(1)N(3)C(1) by –0.22(2) (**I**), 0.59(2) (**II**), and 0.601(5) (**III**) Å and the C(4) atom deviates from the Au(1)N(2)N(4)C(3) plane by 0.657(7) (**I**), –0.58(2) (**II**), and –0.593(5) (**III**) Å. The six-membered delocalized ring AuNCCCN is planar (the average deviation of non-hydrogen atoms from its statistical mean plane is 0.041(3) (**I**), 0.034(8) (**II**), and 0.014(2) (**III**) Å). On the whole, the bond lengths and bond angles of the $[Au(C_9H_{19}N_4)]^{2+}$ cation in complexes **I**–**III** are identical (Table 2). The bond lengths and bond angles of the ClO_4^- and PF_6^- anions correspond to the known values [22, 23].

The crystals of complexes **I**–**III** are not isostructural: they have different unit cell parameters, different symmetries, and different space groups (Table 1). Nevertheless, the detailed analysis of the structures of complexes **I**–**III** indicates a substantial similarity of their packings.

A characteristic feature of packings of the crystal structures of all three complexes is the presence of infinite strips of alternating cations and anions (Figs. 1a–1c) in which the bridging anions $Y(1)^-$ and $Y(2)^-$ bind the "head" and "tail" of the cations to form closed many-membered (14- and 16-membered) rings by cation-anionic hydrogen bonds. From the side of the "head" hydrogen bonds are formed by the H(8A) and H(9B) atoms of the methyl groups of the diiminate rings. The C–H···A bonds are close to linear bonds

(148°–177.5°). From the side of the "tail," the rings are closed by the nonlinear (105.5°–146°) N–H···A bonds of the amine groups. The strips are planar and extended in iodide complex **I** along the *z* axis (Δ = 0.178 Å), in perchlorate complex **II** they are extended along the *xz* diagonal (Δ = 0.194 Å), and in hexafluorophosphate complex **III** they are along the *y* axis (Δ = 0.142 Å) (the root-mean-square deviations (H(C) of perchlorate and hexafluorophosphate were calculated for the non-hydrogen atoms of the cation and the central atoms of the anions). The strips lying in one plane are not bound: the shortest distance is 9.036(1) (**I**), 9.274(1) (**II**), and 8.171(1) (**III**) Å.

The $[Au(C_9H_{19}N_4)]^{2+}$ cations of complexes **I–III** multiplied by symmetry centers 0, 0, 0.5 (**I**), 0.5, 0, 0.5 (**II**), and 0, 0.5, 0 (**III**) form doubled piles in the direction of the short axes (Figs. 2a–2c). Infinite chains of the $Y(1)^-$ and $Y(2)^-$ anions are localized in cavities between the piles.

The cation-cationic interactions C–H···π [24, 25] of the delocalized six-membered rings of the $[Au(C_9H_{19}N_4)]^{2+}$ cation with the H(A) and H(C) atoms of the terminal methyl groups of the higher- and lower-lying centrosymmetric cations are the main factor binding the cations into the doubled piles. It is shown [2, 26] that the vector C–H of the interactions C–H···π can be directed to both all electrons of the π-acceptor system and the individual C–C bond and even to the C atom. In the structures of complexes **I–III**, the C–H vectors are directed to one of the C atoms of the ring (in complexes **I** and **II**) or to the its medium point L (in complex **III**) (Table 3). As a result, infinite chains of two independent cation-cationic C–H···π bonds are formed in the direction of the short axes. In complexes **I** and **II**, the ···C(5)···H(9A)'–C(9)'–H(9C)'···C(5)''··· and ···C(7)···H(8A)'–C(8)'–H(8C)'···C(7)''··· chains are formed from the hydrogen atoms of the methyl groups $C(9)H_3$ and $C(8)H_3$. In complex **III**, both methyl groups of the cation are involved in the ···L(1)···H(9A)'–C(9)'–C(7)'–C(6)'–C(5)'–C(8)'–H(8A)'···L(1)''··· chains. The geometries of the C–H···π interactions in complexes **I–III** are shown in Fig. 3.

In the region of the five-membered rings, the translation-identical cations of the doubled piles are bound by the vertical cation-anionic chains of two independent hydrogen bonds or Au···A contacts. The nitrogen atoms of the amino groups or the carbon atoms of the ethylene groups are bridging atoms in the hydrogen bond chains. In complex **I**, the ···I(1)···H(3B)'–N(3)'–H(3A)'···I(1)'··· chain is formed by the $N(3)H_2$ amino group with the $I(1)^-$ anions (Fig. 4a). The chain is planar (Δ = 0.143 Å), and the hydrogen atoms of the

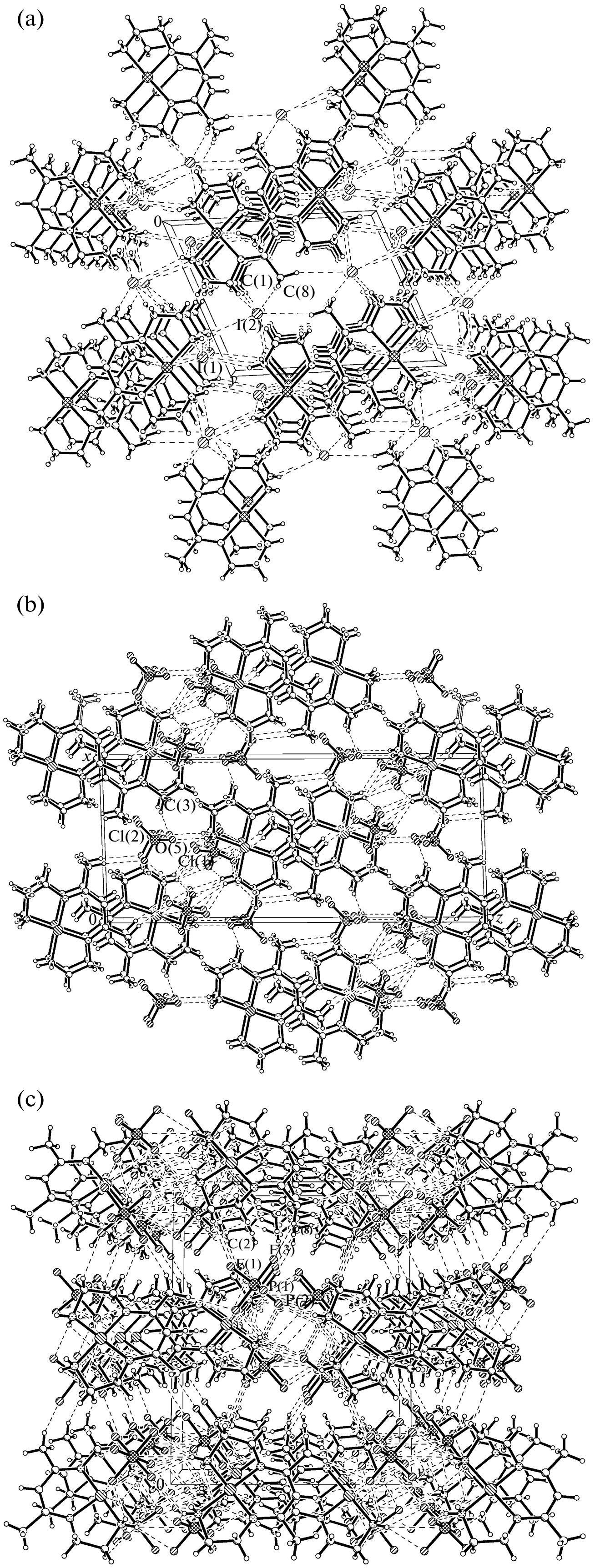

Fig. 2. Projections of the crystal structures on the planes (a) (100) for complex **I**, (b) (010) for complex **II**, and (c) (100) for complex **III**.

Table 3. Geometric parameters of hydrogen bonds and contacts in the structures of compounds **I–III**

D–H···A, Au···A	Distance, Å			Angle DHA, deg	Symmetry transform for A
	D···A	H···A	D–H		
I [9]					
N–H···I					
N(3)–H(3A)···I(1)	3.634(4)	2.963(3)	0.90	133	x, y, z
N(3)–H(3A)···I(2)	3.531(4)	3.164(4)	0.90	109	$-1 + x, y, z$
N(3)–H(3B)···I(2)	3.531(4)	3.145(4)	0.90	108	$-1 + x, y, z$
N(3)–H(3B)···I(1)	3.551(3)	2.809(3)	0.90	141	$-1 + x, y, z$
N(4)-H(4A)···I(2)	3.671(4)	2.919(3)	0.90	142	$2 - x, 2 - y, z$
N(4)-H(4B)···I(1)	3.507(4)	2.712(4)	0.90	148	$2 - x, 2 - y, 2 - z$
C–H···I					
C(1)–H(1A)···I(2)	4.077(6)	3.171(5)	0.97	156	$2 - x, 1 - y, z$
C(1)–H(1B)···I(2)	4.094(6)	3.189(5)	0.97	156	$3 - x, 1 - y, 2 - z$
C(8)–H(8A)···I(2)	4.178(5)	3.23(2)	0.96	170	$3 - x, 1 - y, 2 - z$
C(8)–H(8B)···I(2)	4.060(5)	3.168(9)	0.96	155	$1 + x, y, z$
C(9)–H(9B)···I(1)	3.910(5)	3.063(8)	0.96	148	$2 - x, 2 - y, 1 - z$
C–H···Au					
C(9)–H(9B)···Au(1)	3.964(5)	3.32(3)	0.96	126	$1 - x, 2 - y, 1 - z$
C–H···π					
C(9)–H(9A)···N(1)	3.588(6)	2.96(2)	0.96	124	$1 - x, 2 - y, 1 - z$
C(9)–H(9A)···C(5)	3.498(6)	2.74(2)	0.96	137	$1 - x, 2 - y, 1 - z$
C(9)–H(9A)···C(6)	3.563(6)	3.04(2)	0.96	116	$1 - x, 2 - y, 1 - z$
C(9)–H(9A)···C(7)	3.851(6)	3.64(2)	0.96	95	$1 - x, 2 - y, 1 - z$
C(9)–H(9A)···N(2)	4.060(6)	3.99(2)	0.96	87	$1 - x, 2 - y, 1 - z$
C(9)–H(9A)···L(1)*	3.421(5)	3.01(2)	0.96	107	$1 - x, 2 - y, 1 - z$
C(9)–H(9C)···N(1)	3.774(6)	2.86(1)	0.96	160	$2 - x, 2 - y, 1 - z$
C(9)–H(9C)···C(5)	3.589(7)	2.65(1)	0.96	167	$2 - x, 2 - y, 1 - z$
C(9)–H(9C)···C(6)	3.575(6)	2.81(1)	0.96	137	$2 - x, 2 - y, 1 - z$
C(9)–H(9C)···C(7)	3.716(6)	3.16(2)	0.96	118	$2 - x, 2 - y, 1 - z$
C(9)–H(9C)···N(2)	3.836(6)	3.35(2)	0.96	114	$2 - x, 2 - y, 1 - z$
C(9)–H(9C)···L(1)*	2.979(4)	2.65(1)	0.96	141	$2 - x, 2 - y, 1 - z$
Au···I					
Au(1)···I(1)		3.664(1)			x, y, z
Au(1)···I(1)		3.968(1)			$1 + x, y, z$
II					
N–H···O					
N(3)–H(3A)···O(1)	3.08(2)	2.44(1)	0.90	128	x, y, z
N(3)–H(3A)···O(1)	3.10(2)	2.53(2)	0.90	121	$1/2 - x, y - 1/2, 1/2 - z$
N(3)–H(3A)···O(4)	2.97(2)	2.25(2)	0.90	137	$1/2 - x, y - 1/2, 1/2 - z$
N(3)–H(3B)···O(2)	2.99(2)	2.33(2)	0.90	131	$x, -1 + y, z$
N(3)–H(3B)···O(7)	3.33(2)	2.58(2)	0.90	141	x, y, z
N(4)-H(4A)···O(4)	2.93(2)	2.08(2)	0.90	156	$x, -1 + y, z$
N(4)-H(4B)···O(5)	3.05(2)	2.28(2)	0.90	144	$1/2 - x, y + 1/2, 1/2 - z$
N(4)-H(4B)···O(3)	3.05(2)	2.44(2)	0.90	125	x, y, z
C–H···O					
C(3)–H(3A)···O(5)	3.33(2)	2.54(2)	0.97	139	$1 + x , y, z$
C(3)–H(3B)···O(3)	3.25(2)	2.59(20	0.97	126	x, y, z
C(8)–H(8B)···O(2)	3.28(2)	2.34(3)	0.96	167	$1 - x, 1 - y, 1 - z$
C(9)–H(9B)···O(7)	3.46(2)	2.59(4)	0.96	151	$1 - x, -y, 1 - z$
C–H···π					
C(8)–H(8A)···N(1)	3.99(2)	3.65(8)	0.96	104	$1 - x, 1 - y, 1 - z$
C(8)–H(8A)···C(5)	3.81(2)	3.36(7)	0.96	111	$1 - x, 1 - y, 1 - z$
C(8)–H(8A)···C(6)	3.63(2)	2.91(6)	0.96	133	$1 - x, 1 - y, 1 - z$
C(8)–H(8A)···C(7)	3.71(2)	2.81(6)	0.96	157	$1 - x, 1 - y, 1 - z$
C(8)–H(8A)···N(2)	4.01(2)	3.20(6)	0.96	144	$1 - x, 1 - y, 1 - z$
C(8)–H(8A)···L(1)*	3.61(1)	2.95(6)	0.96	128	$1 - x, 1 - y, 1 - z$
C(8)–H(8C)···N(1)	3.93(2)	3.56(7)	0.96	106	$1 - x, -y, 1 - z$
C(8)–H(8C)···C(5)	3.80(2)	3.32(7)	0.96	113	$1 - x, -y, 1 - z$
C(8)–H(8C)···C(6)	3.72(2)	2.98(6)	0.96	135	$1 - x, -y, 1 - z$
C(8)–H(8C)···C(7)	3.77(2)	2.85(6)	0.96	160	$1 - x, -y, 1 - z$
C(8)–H(8C)···N(2)	3.77(2)	2.93(6)	0.96	147	$1 - x, -y, 1 - z$
C(8)–H(8C)···L(1)*	3.49(1)	2.80(6)	0.96	130	$1 - x, -y, 1 - z$

Table 3. (Contd.)

D–H···A, Au···A	Distance, Å			Angle DHA, deg	Symmetry transform for A
	D···A	H···A	D–H		
Au···O					
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*
III					
N–H···F					
N(3)–H(3A)···F(4)	3.093(4)	2.266(4)	0.90	153	2 − *x*, 1 − *y*, −*z*
N(3)–H(3A)···F(6)	3.147(4)	2.474(4)	0.90	132	2 − *x*, 1 − *y*, −*z*
N(3)–H(3A)···F(4)	2.931(4)	2.559(4)	0.90	106	*x*, −1 + *y*, *z*
N(3)–H(3B)···F(9)	2.996(4)	2.419(4)	0.90	122	*x*, −1 + *y*, *z*
N(3)–H(3B)···F(10)	2.903(3)	2.146(3)	0.90	141	1 − *x*, 1 − *y*, −*z*
N(4)-H(4A)···F(8)	3.021(3)	2.345(4)	0.90	132	1 − *x*, 1 − *y*, −*z*
N(4)-H(4A)···F(5)	3.089(4)	2.349(4)	0.90	140	1 − *x*, 1 − *y*, −*z*
N(4)-H(4B)···F(9)	2.987(4)	2.253(4)	0.90	138	*x*, −1 + *y*, −*z*
N(4)-H(4B)···F(11)	3.018(4)	2.265(4)	0.90	141	*x*, −1 + *y*, −*z*
N(4)-H(4B)···F(2)	2.954(4)	2.538(4)	0.90	109	2 − *x*, 1 − *y*, −*z*
C–H···F					
C(1)–H(1A)···F(7)	3.093(4)	2.432(4)	0.97	125	2 − *x*, 1 − *y*, −*z*
C(2)–H(2A)···F(1)	3.042(5)	2.451(5)	0.97	119	3/2 − *x*, *y* − 1/2, −1/2 − *z*
C(2)–H(2A)···F(12)	3.413(4)	2.528(4)	0.97	152	1 − *x*, 1 − *y*, −*z*
C(4)–H(4A)···F(2)	3.162(5)	2.530(5)	0.97	123	2 − *x*, 1 − *y*, −*z*
C(8)–H(8B)···F(6)	3.449(4)	2.489(6)	0.96	178	*x*, *y*, *z*
C(8)–H(8C)···F(3)	3.356(4)	2.45(1)	0.96	158	3/2 − *x*, *y* −1/2, −1/2 − *z*
C(9)–H(9B)···F(8)	3.396(4)	2.442(7)	0.96	172	*x*, *y*, *z*
C–H···π					
C(8)–H(8A)···N(1)	4.017(4)	3.73(1)	0.96	100	2 − *x*, 1 − *y*, −*z*
C(8)–H(8A)···C(5)	3.647(5)	3.19(1)	0.96	110	2 − *x*, 1 − *y*, −*z*
C(8)–H(8A)···C(6)	3.565(5)	2.81(1)	0.96	136	2 − *x*, 1 − *y*, −*z*
C(8)–H(8A)···C(7)	3.870(5)	3.003(9)	0.96	151	2 − *x*, 1 − *y*, −*z*
C(8)–H(8A)···N(2)	4.193(4)	3.48(1)	0.96	133	2 − *x*, 1 − *y*, −*z*
C(8)–H(8A)···L(1)*	3.658(3)	3.04(1)	0.96	123	2 − *x*, 1 − *y*, −*z*
C(9)–H(9A)···N(1)	3.816(4)	3.04(1)	0.96	139	1 − *x*, 1 − *y*, −*z*
C(9)–H(9A)···C(5)	3.710(5)	2.833(9)	0.96	152	1 − *x*, 1 − *y*, −*z*
C(9)–H(9A)···C(6)	3.657(5)	2.97(1)	0.96	130	1 − *x*, 1 − *y*, −*z*
C(9)–H(9A)···C(7)	3.792(4)	3.40(2)	0.96	107	1 − *x*, 1 − *y*, −*z*
C(9)–H(9A)···L(1)*	3.520(3)	2.91(2)	0.96	123	1 − *x*, 1 − *y*, −*z*
Au···F					
Au(1)···F(2)	3.118(3)				2 − *x*, 1 − *y*, −*z*
Au(1)···F(6)	3.423(3)				2 − *x*, 1 − *y*, −*z*
Au(1)···F(8)	3.175(3)				1 − *x*, 1 − *y*, −*z*
Au(1)···F(10)	3.655(3)				1 − *x*, 1 − *y*, −*z*

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

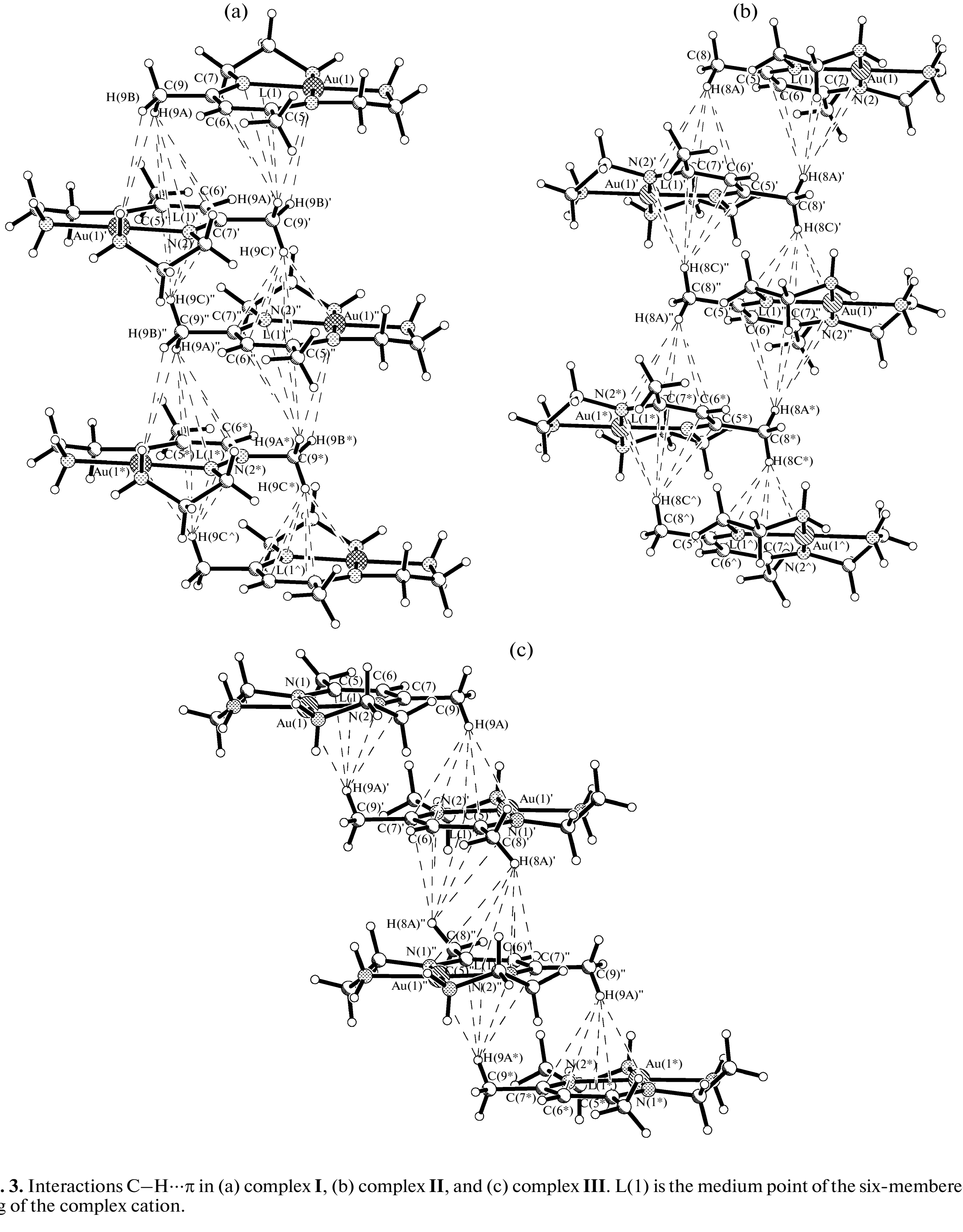

Fig. 3. Interactions C–H···π in (a) complex **I**, (b) complex **II**, and (c) complex **III**. L(1) is the medium point of the six-membered ring of the complex cation.

amino group (H(3A) and H(3B)) are localized along the short axis. The ···Au(1)···I(1)···Au(1)'···I(1)'··· chain of short contacts 3.968(1) and 3.664(1) Å is also formed of the I(1)$^-$ anions. The I(1)···Au(1)'···I(1)' angle is 125.8°, and the sloping angles Au(1)'···I(1) and Au(1)'···I(1)' to the cation plane are 60.6° and 64.4°, respectively. As a result, each cation with the higher- and lower-lying anions I(1)$^-$ forms nearly planar quadrangles I(1)'H(3A)'N(3)'Au(1)' and I(1)H(3B)'N(3)'Au(1)' (Δ = 0.078 and 0.040 Å), having the common edge (Au(1)'N(3)') (Fig. 4a). The cation-anionic chain ···I(2)···H(1A)'–C(1)'–

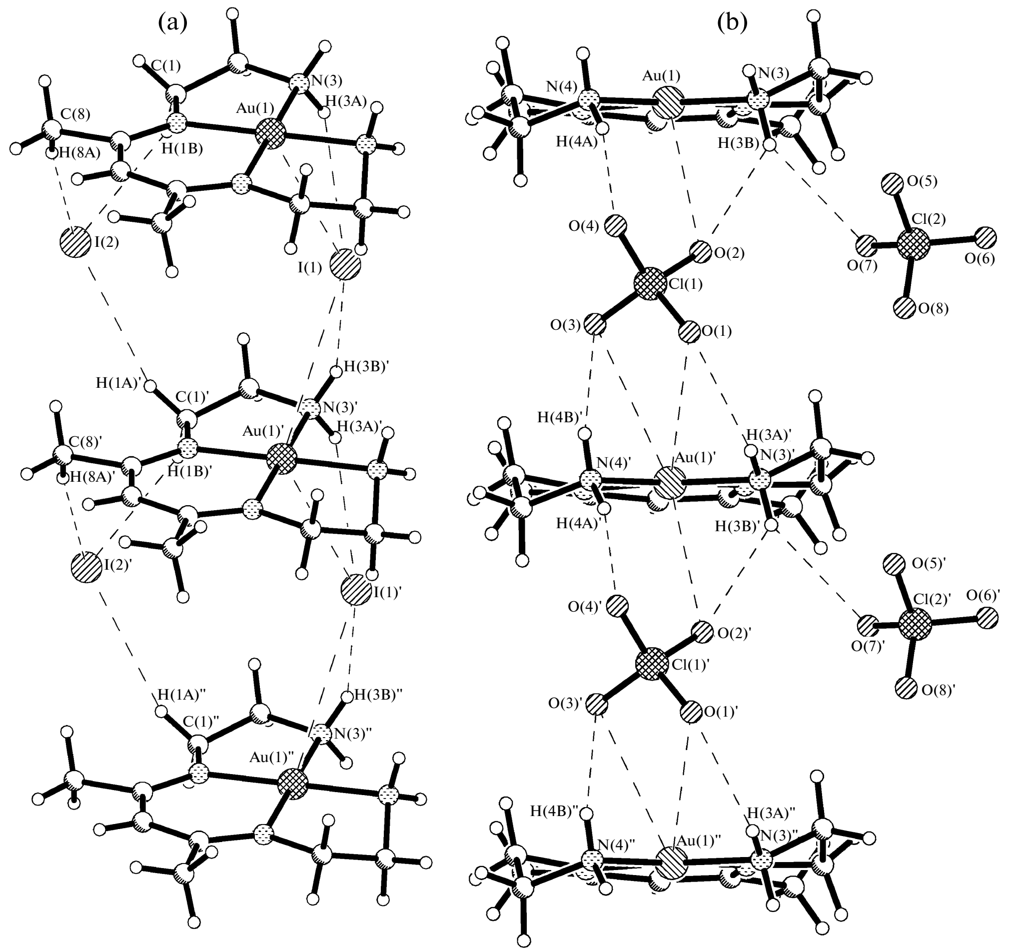

Fig. 4. Chains and rings of hydrogen bonds and contacts in the direction of short axes in (a) complex **I**, (b) complex **II**, and (c) complex **III**.

H(1B)'···I(2)'··· (Δ = 0.059 Å) is formed by both hydrogen atoms of the methylene group $C(1)H_2$ and anions $I(2)^-$. Note that the $I(2)^-$ anions form no contacts with Au: the nearest I(2) atom is remote from the gold atom by 5.255(1) Å.

In complex **II**, all oxygen atoms of the $Cl(1)O_4$ group and all hydrogen atoms of the both amino groups of the cation are involved in the formation of vertical chains of the N–H···O bonds (Fig. 4b, Table 3). The hydrogen atoms of the $N(3)H_2$ group form a chain of hydrogen bonds by the O(1) and O(2) atoms, and the hydrogen atoms of the $N(4)H_2$ group form hydrogen bond chains with the O(3) and O(4) atoms of the anion. Note that the chain fragments O···H–N–H···O lie in the plane: for O(1)···H(3A)'–N(3)'–H(3B)'···O(2)' Δ = 0.152 Å, and for O(3)···H(4B)'–N(4)'–H(4A)'···O(4)' Δ = 0.134 Å. The gold atoms are bound to the O(1), O(2), and O(3) atoms by short contacts Au···O also forming the chains ···Au(1)···O(2)–Cl(1)–O(1)···Au(1)'··· and ···Au(1)···O(2)–Cl(1)–O(3)···Au(1)'···, and the sloping angles Au(1)'···O(2)', Au(1)'···O(3), and Au(1)'···O(1) to the plane of the cation are 64.6°, 64.5°, and 48.9°, respectively. As a result, planar four-membered rings AuNHO are formed as for the iodide complex (Δ = 0.110 Å for Au(1)'N(3)'H(3A)'O(1); Δ = 0.044 Å for Au(1)'N(3)'H(3B)'O(2)', and Δ = 0.097 Å for Au(1)'N(4)'H(4B)'O(3)). The dihedral angle between the planes of the Au(1)'N(3)'H(3A)'O(1) and Au(1)'N(4)'H(4B)'O(3) quadrangles is 99.5°, i.e., close to the N(3)Au(1)N(4) angle of the cation equal to 98.2°. The central gold atom of the cation has no short contacts with the $Cl(2)O_4^-$ anion: the shortest distance to the O(7) oxygen atom is 4.61(2) Å.

In the hexafluorophosphate complex (Fig. 4c), the cations translation-identical along the *x* axis are also penetrated by two infinite chains of hydrogen bonds. In the former ···F(2)–P(1)–F(5)···H(4A^)–N(4)'–H(4B)'··· chain, the N(4) nitrogen atoms of the cations and the $P(1)F_6^-$ anions are bridging. The latter ···F(7)–P(2)–F(12)···H(2A)'–C(2)'–C(1)'–H(1A)'··· chain is formed by the $–C(1)H_2–C(2)H_2–$ ethylene groups and the $P(2)F_6^-$ anions. The chain fragments F···H–N–H···F and F···H–C–C–H···F are nearly

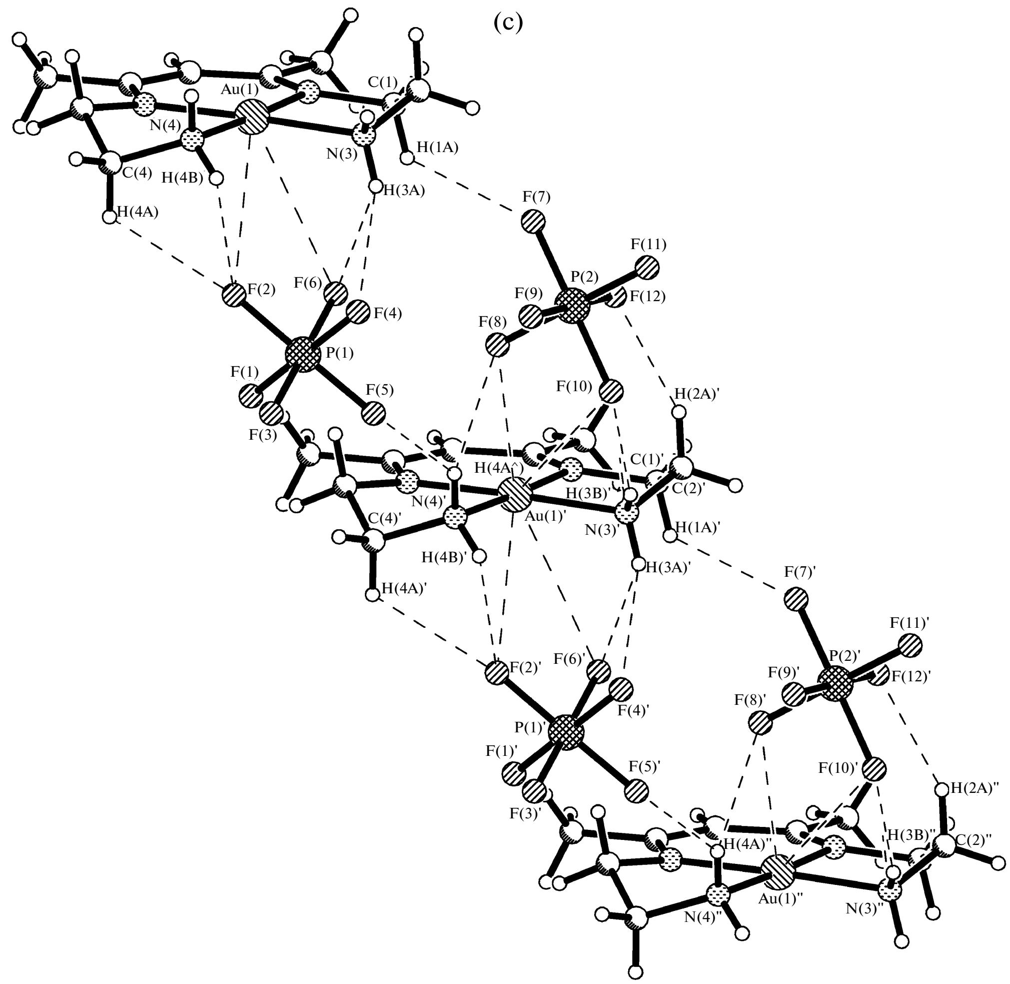

Fig. 4. (Contd.)

planar (Δ = 0.191 and 0.145 Å, respectively). The Au atom has four contacts Au···F: two contacts with the higher-lying $P(1)F_6^-$ anion (the sloping angles Au(1)···F(2) and Au(1)···F(6) to the cation plane are 62.9° and 65.9°, respectively) and two contacts with the lower-lying anion $P(2)F_6^-$ (the sloping angles Au(1)···F(8) and Au(1)···F(10) to the cation plane are 67.7° and 40.7°). The AuNHF quadrangles formed by the N–H···F bonds and Au···F contacts of the cation and anions are nearly planar as for iodide and perchlorate: for Au(1)N(4)H(4B)F(2) Δ = 0.163 Å, for Au(1)N(3)H(3À)F(6) Δ = 0.078 Å, for Au(1)'N(4)'H(4A)'F(8) Δ = 0.015 Å, and for Au(1)'N(3)'H(3B)'F(10) Δ = 0.099 Å. The dihedral angle between the planes of the Au(1)N(3)H(3A)F(6) and Au(1)N(4)H(4B)F(2) quadrangles formed by the bonds and contacts of the cation with the F(6) and F(2) atoms of the $P(1)F_6^-$, anion (98.6°) is close to the value of the N(3)Au(1)N(4) angle of the cation equal to 97.4°). Note that there are no vertical chains of the Au···F contacts in hexafluorophosphate complex **III**, unlike complexes **I** and **II** with I^- and ClO_4^-. As a whole, in the direction of the short axis the doubled piles of cations are penetrated by several zigzag cation-cationic and cation-anionic chains directed up and down from the cation plane and joining the cations into piles to form a supramolecular structural motif.

Note that in complex **III** the bonds of the anions with the higher- and lower-lying cations are unequal: $P(1)F_6^-$ has only one bond (N(4)'–H(4A^)···F(5)) with the lower-lying cation, whereas six bonds and contacts are observed with the lower-lying cation. On the contrary, the $P(2)F_6^-$ anion is closely bound to the lower-lying cation (five hydrogen bonds and contacts), and only the C(1)–H(1A)···F(7) bond with the higher-lying cation is observed (Table 3, Fig. 4c). Thus, each cation in the pile in the region of five-membered rings has eleven cation-anionic hydrogen bonds and Au···F contacts with the higher- and lower-lying anions $P(1)F_6^-$ and $P(2)F_6^-$ to form a pseudomolecular triad

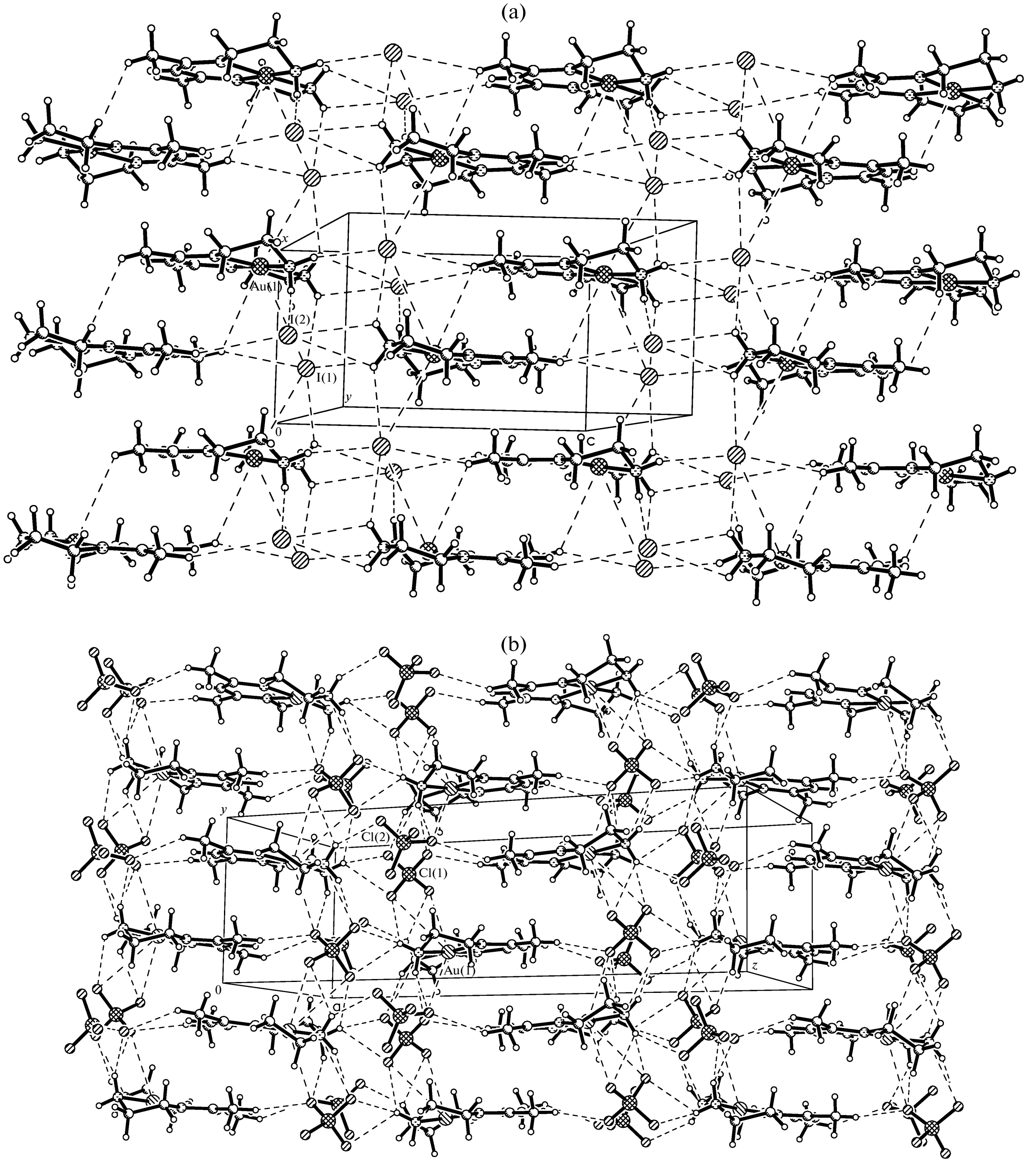

Fig. 5. View of the layer of cations and anions perpendicular to the plane (a) (010) for complex **I**, (b) $(\bar{1}01)$ for complex **II**, and (c) (001) for complex **III**.

translation-identical in the direction of the short *x* axis.

Since the cations translation-identical in the short direction are penetrated by more than one chain of hydrogen bonds or contacts, along this direction there are the translation-identical rings "one cation–one anion" (**I–III**) and "two cations–two anions" (**I** and **III**) (Figs. 4a–4c). The rings "one cation–one anion" form either two independent hydrogen bonds, or one hydrogen bond and one contact, or two contacts; and the rings "two cations–two anions" are formed by four independent hydrogen bonds or two hydrogen bonds and two contacts.

The doubled piles of cations are tightly bound in the region of amino groups by the closed rings formed by four hydrogen bonds N–H···A of two centrosym-

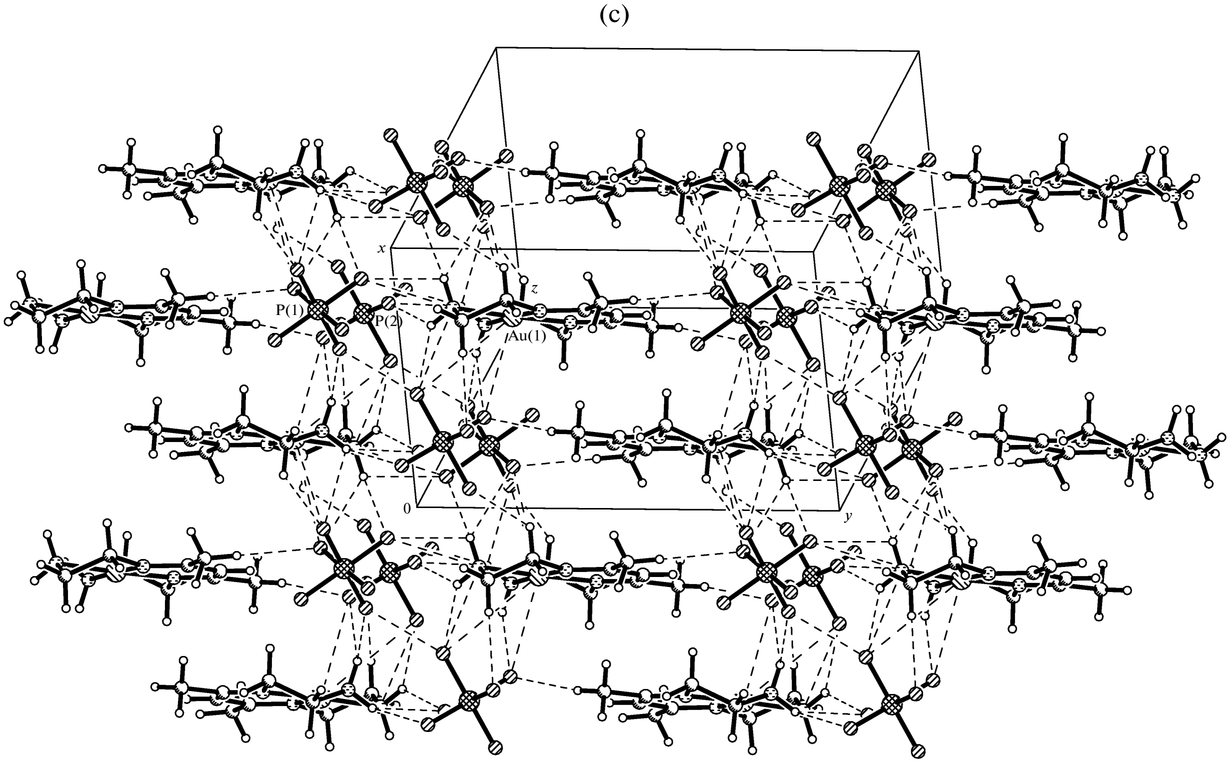

Fig. 5. (Contd.)

metric cations of adjacent piles and pairs of the nearest anions ($Y(1)^- + Y(1)^-$, $Y(2)^- + Y(2)^-$, $Y(1)^- + Y(2)^-$ for complexes **I** and **III**; $Y(1)^- + Y(1)^-$, $Y(1)^- + Y(2)^-$ for complex **II**). The rings are extended along the short axes to form columns (Figs. 5a–5c). In the case of the same anions ($Y(1)^- + Y(1)^-$, $Y(2)^- + Y(2)^-$), the rings are symmetric and formed by two pairs of independent hydrogen bonds. In the case of different anions ($Y(1)^- + Y(2)^-$), the rings include four independent hydrogen bonds.

Since each cation participates by the C–H···A bonds of the methyl groups in the formation of infinite strips in the directions *z* (**I**), *xz* (**II**), and *y* (**III**), the doubled piles of cations are bound in the planes (010) (**I**), $(\bar{1}01)$ (**II**), and (001) (**III**) into dimeric layers (Figs. 2 and 5) in which the most part of hydrogen bonds and contacts is concentrated. The bond between the layers (C–H···A) are formed by the methyl and methylene groups of the cation with one of the anions (in complex **I** with $I(2)^-$: C(8)–H(8A)···I(2), C(1)–H(1A)···I(2), C(1)–H(1B)···I(2); in complex **II** with $Cl(2)O_4^-$: C(3)–H(3A)···O(5); in complex **III** with $P(1)F_6^-$: C(8)–H(8C)···F(3) and C(2)–H(2A)···F(1) (Figs. 2a–2c, Table 3).

It is remarkable that in the packing of the structure the hydrogen atoms of the methyl groups perform different functions. The H(9A) and H(9C) atoms in complex **I**, H(8A) and H(8C) in complex **II**, and H(8A) and H(9A) in complex **III** bind the cations into the piles. The H(8B) and H(9B) atoms of all three complexes bind the cations into the strips (and into the layers), and the atoms H(8A) in **I** and H(8C) in complex **III** along with the methylene group of the five-membered ring form hydrogen bonds between the layers.

Thus, the crystal structures of complexes **I**–**III** contain a wide network of cation-anionic and cation-cationic secondary interactions (hydrogen bonds D–H···A and short contacts Au···A) (Table 3), which makes it possible to present the crystal packing as a three-dimensional framework. Each cation in complexes **I**–**III** is bound with two cations and seven to nine anions. Each anion is bound with four to five cations. The gold atoms of the cations are not bound: the closest distance between them is 6.795(1) (**I**), 6.888 (**II**), and 7.125(2) (**III**) Å.

The amine, methyl, and methylene groups of the cations are donors of hydrogen bonds. The anions, delocalized six-membered ring, and central gold atom (for complex **I**) are acceptors. Following Jeffrey's typology [14], the hydrogen bonds of the hexafluorophosphate (**III**) and perchlorate (**II**) complexes can be classified as medium and weak, and those of the iodide complex (**I**) can be classified as weak bonds. Among the cation–anionic hydrogen bonds, the amine group forms the shortest bonds (2.08(2) Å in complex **II**), and the C–H···A bond lengths of the methyl and methylene groups in all complexes are approximately equal (3.06–3.23 Å). The shortest cation–cationic bonds C–H···π (2.65(1), 2.74(2) Å) are observed for iodide complex **I**, and they are approximately equal in length (~2.8 Å) for the perchlorate (**II**) and hexafluorophosphate (**III**) complexes.

The structures of all three complexes include bi- and trifurcate hydrogen bonds (Table 3). In iodide complex **I**, the three-centered hydrogen bonds are formed by both hydrogen atoms of the N(3)H_2 group and one of the hydrogen atoms ("strip" atom) of the C(9)H_3 methyl group. In perchlorate **II** (four acceptor atoms at the anion), two atoms (H(3B) and H(4B)) of the amino groups form three-centered and one (H(3A)) form the four-centered hydrogen bond. In hexafluorophosphate complex **III** (six acceptor atoms at the anion), two hydrogen atoms of the amino groups form three-centered hydrogen bonds and two atoms form four-centered hydrogen bonds. The three-centered bifurcate hydrogen bond is also formed by the H(2A) atom of the C(2)H_2 methylene group (Table 3). The three- and four-centered hydrogen bonds are nonsymmetric and have the main component with the shorter H···A bond and larger DHA angle. The three-centered hydrogen bonds in complexes **I**–**III** are almost planar. In complex **I**, the deviation of the atoms from their root-mean-square plane (Δ) for the N(3)–H(3A)···I(1),I(2) bond is 0.035 Å, for N(3)–H(3B)···I(1),I(2) Δ = 0.024 Å, and for C(9)–H(9B)···I(1),Au(1) Δ = 0.076 Å. In complex **II**, for N(3)–H(3B)···O(2),O(7) Δ = 0.082 Å and for N(4)–H(4B)···O(5),O(3) Δ = 0.029 Å. In complex **III**, for N(3)–H(3B)···F(9),F(10), N(4)–H(4A)···F(5),F(8), C(2)–H(2A)···F(1),F(12) Δ = 0.071, 0.058, and 0.021 Å, respectively. The four-centered hydrogen bonds are nonplanar.

The hydrogen atoms of the amino groups of complexes **I**–**III** form chelate bonds N–H(H)···A in iodide complex **I** (Fig. 1a). The polyatomic anions ClO_4^- in complex **II** and PF_6^- in complex **III** form chelate bonds H···A(A)–X (Figs. 1b, 1c, and 4c). The quadrangles of the chelate bonds are nearly planar for complexes **I** and **II** (Δ = 0.092 Å for H(3A)N(3)H(3B)I(2)) and 0.091 Å for H(3A)O(1)Cl(1)O(4)) and somewhat deviate from the plane for complex **III** (Δ = 0.209 Å for H(4B)F(9)P(2)F(11) and Δ = 0.170 Å for H(3A)F(6)P(1)F(4)).

The anions of the complexes also form multicentered hydrogen bonds. In complex **I**, the $I(1)^-$ and $I(2)^-$ ions form four and seven hydrogen bonds. In complex **II**, each oxygen atom of the $Cl(1)O_4^-$ anion and the O(5) and O(7) atoms of the $Cl(2)O_4^-$ anion have two hydrogen bonds each. In complex **III**, five of twelve fluorine atoms (F(2), F(4), F(6), F(8), and F(9)) form two hydrogen bonds each. As a whole, complexes **II** and **III** with the polyatomic ClO_4^- and PF_6^- anions have more intermolecular bonds and contacts than complex **I** with monoatomic I^- (13 in **I**, 15 in **II**, and 21 in **III**).

It should be noted in conclusion that the isolated complex cations $[Au(C_9H_{19}N_4)]^{2+}$ and anions Y^- joined into a three-dimensional framework by hydrogen bonds and contacts form the basis of the crystal structure of the gold(III) iminate–amine complexes $[Au(C_9H_{19}N_4)]Y_2$ (Y = I, ClO_4, and PF_6). The planar acyclic cation, whose structure provides a possibility to form numerous classical and nonclassical cation-cationic and cation-anionic hydrogen bonds, plays the decisive role in the formation of structures of complexes **I**–**III**. The replacement of the anion does not basically change the packing. Its characteristic features (doubled piles of cations and chains of anions along the short axis) remain the same along with the totality of secondary interactions (hydrogen bonds N–H···A, C–H···A, C–H···Au, C–H···π and short contacts Au···A (A = I, O, and F)) that determine and stabilize the packing.

The regularities of mutual arrangement of ions and the geometry of hydrogen bonds and contacts in the structures of complexes **I**–**III** are similar. The predominant part of cation-anionic intermolecular interactions is formed by the classical hydrogen bonds N–H···A and is concentrated along the short axes in the region of five-membered rings (more exactly, amino groups): the chains of hydrogen bonds and contacts are extended along these axes and the closed cation-anionic rings are multiplied along them by the symmetry centers and translations. In the same direction the cations are bound by the cation-cationic interactions of π electrons of the six-membered delocalized rings with the terminal methyl groups. The nonclassical C–H···A bonds of the methyl and methylene groups form a three-dimensional network in the structures of complexes **I**–**III**.

REFERENCES

1. Desiraju, G.R. and Steiner, T., *The Weak Hydrogen Bond in Structural Chemistry and Biology*, New York: Oxford University, 1999.
2. Steiner, T., *Angew. Chem., Int. Ed. Engl.*, 2002, vol. 41, no. 1, p. 48.
3. Friedrichs, S. and Jones, P.G., *Z. Naturforsch.*, 2004, vol. 59b, p. 49.
4. Zhao, H.-Y., Qiu, X.H., Xie, Y.-B., and Shen, P.-W., *J. Mol. Struct.*, 2005, vol. 733, nos. 1–3, p. 95.
5. Zhao, Y.J., Hong, M.C., Liang, Y.C., et al., *Polyhedron*, 2001, vol. 20, p. 2619.
6. Su, W.P., Hong, M.C., Weng, J.B., et al., *Inorg. Chim. Acta*, 2002, vol. 331, p. 8.
7. Tiekink, R.T., *Gold Bull*, 2003, vol. 36, no. 4, p. 117.
8. Afanas'eva, V.A., Mironov, I.V., Glinskaya, L.A., and Klevtsova, R.F., *Russ. J. Coord. Chem.*, 2010, vol. 36, no. 1, p. 9.

9. Afanas'eva, V.A., Glinskaya, L.A., and Korol'kov, I.V., *Russ. J. Coord. Chem.*, 2012, vol. 38, no. 8, p. 526.
10. Afanas'eva, V.A., Baidina, I.A., Mironov, I.V., et al., *Zh. Strukt. Khim.*, 2000, vol. 41, no. 5, p. 1019.
11. Block, B.P. and Bailar, J.C., *J. Am. Chem. Soc.*, 1951, vol. 73, no. 10, p. 4722.
12. Brawner, S.A., Lin, I.J.B., Kim, J.-H., et al., *Inorg. Chem.*, 1978, vol. 17, no. 5, p. 1304.
13. Sheldrick, G.M., *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, vol. 64, no. 1, p. 112.
14. Jeffrey, G.A., *An Introduction to Hydrogen Bonding*, New York-Oxford: Oxford University, 1997.
15. Desiraju, G.R., *Acc. Chem. Res.*, 1996, vol. 29, no. 9, p. 441.
16. Braga, D. and Grepioni, F., *Acc. Chem. Res.*, 2000, vol. 33, no. 9, p. 601.
17. Grepioni, F., Cojazzi, G., Draper, S.M., et al., *Organometallics*, 1998, vol. 17, no. 3, p. 296.
18. Kovács, A., *Coord. Chem. Rev.*, 2006, vol. 250, nos. 5–6, p. 710.
19. Janczak, J. and Perpetuo, G.J., *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2007, vol. 63, no. 2, p. 117.
20. Antunes, O.A.C., Bordinhao, J., Carvalho, N.M.F., et al., *J. Chem. Crystallogr.*, 2007, vol. 37, no. 4, p. 291.
21. Liu, F., Chen, W., and You, X., *J. Chem. Crystallogr.*, 2002, vol. 32, nos. 1–2, p. 27.
22. Kofod, P. and Harris, P., *Inorg. Chem.*, 2004, vol. 43, no. 8, p. 2680.
23. Hess, C.R., Weyhermuller, T., Bill, E., et al., *Inorg. Chem.*, 2010, vol. 49, no. 12, p. 5686.
24. Bogdanović, G.A., Spasojević-de Biré, A., Zarić, S.D. *Eur. J. Inorg. Chem*. 2002. no. 7. P. 1599.
25. Suezawa, H., Yoshida, T., Umezawa, Y., et al., *Eur. J. Inorg. Chem.*, 2002, no. 12, p. 3148.
26. Steiner, T., Mason, S.A., and Tamm, M., *Acta Crystallogr., Sect. B: Struct. Sci.*, 1997, vol. 53, no. 5, p. 843.