Synthesis and Crystal Structure of Dimethylgold(III) Carboxylates

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Abstract—Three novel carboxylate complexes were synthesized: dimethylgold(III) trifluoroacetate $[Me_2Au(Tfa)]_2$ (I), trimethylacetate (pivalate) $[Me_2Au(Piv)]_2$ (II), and benzoate $[Me_2Au(OBz)]_2$ (III). The starting reagent was $[Me_2Au]_2$. The procedure of its synthesis provides 60% product yield. Dimethylgold(III) carboxylates were identified from the IR and ¹H NMR data. The title compounds were studied by X-ray diffraction. The unit cell parameters for I, $C_8H_{12}Au_2F_6O_4$: a = 15.5522(13), b = 12.9398(11), c = 15.6555(14) Å, $\beta = 104.308(2)^\circ$, Z = 8, $\rho(\text{calcd.}) = 2.959$ g/cm³, space group C2/c, R = 0.0779; for II, $C_{14}H_{30}Au_2O_4$: a = 10.3025(3), b = 15.5952(4), c = 12.6819(3) Å, $\beta = 105.8270(10)^\circ$, Z = 4, $\rho(\text{calcd.}) = 2.224$ g/cm³, space group $P2_1/c$, R = 0.0229; for III, $C_{18}H_{22}Au_2O_4$: a = 12.8050(2), b = 19.7886(3), c = 7.60300(10) Å, Z = 4, $\rho(\text{calcd.}) = 2.401$ g/cm³, space group Pnma, R = 0.0144. Compounds I–III have the molecular structures; the structural units are the [(CH₃)₂Au(OOCR)]₂ dimers (Au···Au 2.984–3.080 Å), $R = CF_3$, *tert*-Bu, Ph. The gold atoms have the square coordination with two carbon atoms and two oxygen atoms (Au–O 2.120–2.173 Å). The molecules in compounds I–III are united into infinite unidimensional chains connected by van der Waals interactions.

DOI: 10.1134/S1070328408010119

The gold complexes with the organic ligands are used in plating of the functional gold-containing coatings and films by the chemical vapor deposition method [1, 2]. The data on the synthesis procedures and structures of the organic complexes of gold will simplify the choice of compounds for their practical use.

Previously, we studied the crystal chemical and thermal properties of dimethylgold(III) acetate, $[Me_2Au(OAc)]_2$ (**IV**) [3]. This work continues our investigations of a series of dimethylgold(III) carboxylates and describes the synthesis and X-ray diffraction data on the crystal structure of dimethylgold(III) trifluoroacetate $[Me_2Au(Tfa)]_2$ (**I**), pivalate $[Me_2Au(Piv)]_2$ (**II**), and benzoate $[Me_2Au(OBz)]_2$ (**III**). The above compounds have been synthesized for the first time.

EXPERIMENTAL

The title compounds were synthesized from the corresponding silver carboxylates and dimethylgold(III) iodide. Silver carboxylates were prepared by the reaction of Ag₂O with RCOOH, where $R = CF_3$, *tert*-Bu, Ph [4].

Synthesis of $[Me_2AuI]_2$. A weighed sample of KAuCl₄ (1.00, 2.65 mmol) that was previously dried in a vacuum was added with stirring to a solution of MeLi (10.6 mmol) in 70 ml of hexane and 40 ml of absolute

diethyl ether cooled to -30° C. The reaction was performed in the flow of argon. The reaction mixture was slowly heated to -10° C for 30 min and treated with glacial water acidified with HCl. The organic fraction was separated, an aqueous fraction was extracted with the large quantity of hexane. After the solvents had been distilled off, the product was purified by recrystallization from hexane. The product yield 0.56 g (60%).

Synthesis of $[Me_2AuOOCR]_2$ (R = CF₃ (I), *tert*-Bu (II), Ph (III)). The equimolar amount of $[Me_2AuI]_2$ dissolved in toluene was added with stirring to a mixture of RCOOAg in toluene. The reaction was performed at room temperature for 1 h in continuous argon flow. The reaction mixture was filtered to separate the precipitate formed, and the solvent was evaporated without heating. The product was purified by recrystallization from hexane at $-10^{\circ}C$.

Compound I forms colorless crystals (mp = $102-103^{\circ}$ C).

The IR spectrum (v, cm⁻¹): 3007, 2914, 2808, 1677, 1434, 1213, 1134, 838, 805, 725, 517, 479. The ¹H NMR spectrum (δ , ppm): 1.37 s (Au–CH₃).

Compound II forms colorless crystals (mp = $75-76^{\circ}$ C).

No	Empirical formula	Сс	Content (found/calcd.), %				
110.	Empiredi formula	С	Н	F			
I	$C_8H_{12}Au_2F_6O_4$	14.15/14.13	1.80/1.78	16.89/16.76	90		
II	$C_{14}H_{30}Au_2O_4$	26.45/25.62	4.58/4.61		94		
III	C ₁₈ H ₂₂ Au ₂ O ₄	32.39/32.54	3.48/3.34		78		

 Table 1. The elemental analysis of dimethylgold carboxylates I–III

The IR spectrum (v, cm⁻¹): 2960, 2917, 2869, 1554, 1482, 1414, 1375, 1360, 1231, 1213, 829, 784, 616, 433. The ¹H NMR spectrum (δ , ppm): 1.10 s (Au–CH₃), 1.12 c. (CH₃).

Compound **III** occurs as white crystals (mp = $185-187^{\circ}$ C) and melts with decomposition.

The IR spectrum (v, cm⁻¹): 2995, 2915, 2802, 1595, 1552, 1396, 1237, 1221, 1171, 1069, 1026, 834, 714, 688, 596, 473. The ¹H NMR spectrum (δ , ppm): 1.28 s (Au–CH₃), 7.32–8.03 m (C₆H₅).

Complexes I–III are readily soluble in many organic solvents and are stable at room temperature for several weeks. The powder X-ray diffraction data for I–III confirm single-phase nature of the products. The single crystals for X-ray diffraction were grown by crystallization from hexane. Complexes I, II crystallize as colorless plates belonging to the monoclinic crystal system. Crystals III belong to the rhombic crystal system. The product yields and the chemical analysis data are given in Table 1.

The elemental analysis was performed on the Carlo Erba 1106 analyzer; the error of the C, H determination was 0.3% and 0.5% for halogen determination.

The IR spectra were recorded on a SPECORD 75IR instrument at $400-4000 \text{ cm}^{-1}$ (KBr pellets).

The ¹H NMR spectra were recorded on a MSL 300 instrument (Bruker) with the CDCl₃ solvent and CHCl₃ ($\delta_{\rm H}$ 7.24 ppm) used as the internal standard.

The powder X-ray diffraction analysis of compounds I–III was performed on a DRON-3M diffractometer (Cu K_{α} radiation) in the range of angles $2\theta = 5^{\circ}-50^{\circ}$ at room temperature.

X-ray diffraction analysis. The unit cell parameters and the experimental intensities for refinement of crystal structures **I–III** were measured at 123–150 K on an automated four-circle Bruker-Nonius X8Apex diffractometer equipped with a two-coordinate CCD detector (Mo K_{α} radiation, graphite monochromator). The crystallographic parameters of complexes **I–III** and summary of data collection are given in Table 2. The structure was solved by the heavy atom method and refined in the anisotropic-isotropic (for the H atoms) approximation; the positions of the hydrogen atoms were determined geometrically.

The coordinates and the thermal parameters of the basis atoms are listed in Table 3, the main bond lengths and the bond angles are presented in Table 4. The calculations were performed with the SHELX-97 program package [5]. The X-ray diffraction pictures of the compounds under consideration were fully indexed using the results of the single crystal studies.

RESULTS AND DISCUSSION

It is common practice to use $[Me_2AuX]_2$ (X = Cl, Br, I) as the starting reagents in the synthesis of the most dimethyl-substituted complexes of gold(III) with the organic ligands [6, 7]. The main methods of the synthesis of dimethylgold(II) halides include the interaction of MeLi with AuX₃ [8, 9] or HAuCl₄ [10], the reaction of MeMgX with KAuCl₄ [11], AuX₃, with pyridine-substituted halides of gold [12, 13], and the synthesis from HAuCl₄ and SnMe₄ [14]. The product yield in the above methods does not exceed 40–50%.

In this work, we synthesized the novel organic complexes of gold I-III using dimethylgold(III) iodide as the starting reagent. Previously, [Me₂AuI]₂ was prepared from AuCl₃Py and MeMgI with the yield of 21% [12] and 35% [15]. The authors of [13] performed the reaction of the Grignard reagent with [AuCl₃(R-Py)] (R = Alk) and increased the yield of dimethylgold iodide to 43-45%; the variation of the alkyl radical produced insignificant effect on the product yield. The best results have been achieved by the reaction of the Grignard reagent with KAuCl₄ (50–55%) [11, 16]. The variation of the reaction conditions we performed here did not increase the product yield [3]. In this paper, we suggested the procedure of the synthesis, where the interaction of methyllithium with KAuCl₄ gives dimethylgold iodide in 60% yield. The reagents were mixed at

Parameter	Value					
i arameter	Ι	Ш	III			
М	680.11	656.32	696.29			
Crystal system	Monoclinic	Monoclinic	Rhombic			
Space group	<i>C</i> 2/c	P2 ₁ /c	Pnma			
<i>a</i> , Å	15.5522(13)	10.3025(3)	12.8050(2)			
b, Å	12.9398(11)	15.5952(4)	19.7886(3)			
<i>c</i> , Å	15.6555(14)	12.6819(3)	7.60300(10)			
β, deg	104.308(2)	105.8270(10)	90			
<i>V</i> , Å ³	3052.8(5)	1960.35(9)	1926.55(5)			
Ζ	8	4	4			
ρ (calcd.), g/cm ³	2.959	2.224	2.401			
μ, mm ⁻¹	19.271	14.959	15.229			
<i>F</i> (000)	2432	1216	1280			
Range of θ , deg	2.07-32.64	2.05-30.48	2.87-32.58			
Range of indices	$-16 \le h \le 23,$ $-13 \le k \le 19,$ $-23 \le l \le 23$	$\begin{array}{l} -14 \leq h \leq 14, \\ -22 \leq k \leq 22, \\ -9 \leq l \leq 17 \end{array}$	$-19 \le h \le 11,$ $-29 \le k \le 29,$ $-11 \le l \le 9$			
Number of reflections	12996	18055	19324			
Number of independent reflections; $R_{\rm int}$	5290; 0.0548	5848; 0.0250	3600; 0.0229			
Number of reflections with $I > 2\sigma(I)$	3941	4342	3268			
Number of refined parameters	186	192	156			
GOOF	1.110	1.030	1.029			
<i>R</i> for reflections with $I > 2\sigma(I)$	$R_1 = 0.0779$ $wR_2 = 0.2329$	$R_1 = 0.0229$ $wR_2 = 0.0527$	$R_1 = 0.0144$ $wR_2 = 0.0309$			
<i>R</i> for all reflections	$R_1 = 0.1053$ $wR_2 = 0.2456$	$R_1 = 0.0394$ $wR_2 = 0.0555$	$R_1 = 0.0188$ $wR_2 = 0.0321$			
Residual electron density (min/max), $e/Å^3$	8.063/-5.614	0.914/-0.700	0.938/-1.122			

 Table 2. The crystallographic parameters and summary of data collection for compounds I–III

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	x	v	Ŋ	$U_{ m eq}, { m \AA}^2$	Atom	x	у	Ŋ	$U_{ m eq}, { m \AA}^2$	Atom	x	у	Ŋ	$U_{ m eq},{ m \AA}^2$
		-					Π					III		
2215	.0(5)	2445.8(5)	1000.2(5)	271(2)	Au(1)	6251.0(1)	2159.1(1)	3665.6(1)	234.0(5)	Au(1)	534.56(8)	2500	1975.8(1)	179.6(3)
67	7.2(5)	2308.7(5)	2247.5(5)	270(2)	Au(2)	6332.0(1)	2164.3(1)	1297.0(1)	227.1(5)	Au(2)	2850.03(8)	2500	2424.3(1)	188.0(3)
.66	3(10)	1980(13)	73(10)	360(3)	0(1)	7092(4)	3387(2)	3519(2)	398(8)	O(1)	773.5(12)	3265.3(10)	3923(3)	405(5)
14	1(9)	1691(12)	1035(9)	360(3)	O(2)	7482(3)	3290(2)	1886(2)	357(8)	O(2)	2496.3(12)	3242.5(8)	4364(2)	351(4)
30	7(10)	1700(12)	293(11)	230(3)	C(1)	7562(4)	3656(3)	2772(3)	240(8)	C(1)	1593.6(15)	3454.0(9)	4669(3)	205(4)
44	3(13)	1352(16)	-468(13)	330(4)	C(2)	8353(4)	4503(3)	3005(3)	266(9)	C(2)	1485.3(15)	3995.7(9)	6041(2)	192(3)
6,	53(9)	3833(12)	1713(10)	350(3)	O(3)	4314(3)	2664(3)	2896(3)	413(9)	C(3)	2349.0(16)	4186.5(10)	7044(3)	228(4)
169	98(12)	3993(11)	937(11)	390(3)	O(4)	4520(3)	2851(2)	1196(2)	329(7)	C(4)	2256.8(19)	4706.0(11)	8263(3)	288(4)
106	59(15)	4306(13)	1270(13)	320(4)	C(3)	3909(4)	2930(3)	1936(4)	290(9)	C(5)	1314.3(19)	5037.9(11)	8470(3)	317(5)
8	49(14)	5460(15)	1105(16)	420(6)	C(4)	2539(4)	3388(3)	1620(4)	334(11)	C(6)	449(2)	4841.9(12)	7495(3)	300(5)
) V	71(14)	545(14)	-257(15)	780(6)	C(21)	9742(4)	4274(3)	3773(4)	347(11)	C(7)	533.1(16)	4319.8(10)	6283(3)	241(4)
T	74(15)	970(3)	-1125(15)	1130(11)	C(22)	7621(5)	5131(3)	3577(4)	406(12)	C(1M)	211(2)	3206.3(16)	134(4)	415(7)
-10	22(18)	2072(14)	-731(18)	1350(14)	C(23)	8524(5)	4905(3)	1956(4)	408(12)	C(2M)	3209(2)	3210(2)	621(5)	520(9)
õ	80(2)	5756(12)	311(13)	1130(11)	C(41)	1480(5)	2764(3)	1842(5)	491(14)					
14(02(11)	6006(11)	1662(11)	610(5)	C(42)	2151(6)	3690(5)	443(4)	638(19)					
.,	59(15)	5688(15)	1180(2)	1100(10)	C(43)	2660(5)	4174(3)	2390(5)	483(13)					
27:	58(18)	1014(17)	1032(19)	470(6)	C(1M)	8084(5)	1656(4)	4383(3)	402(13)					
33:	53(19)	2920(2)	1799(17)	500(6)	C(2M)	5424(5)	1055(3)	3997(4)	429(12)					
16	39(11)	2899(19)	3385(12)	360(4)	C(3M)	8035(4)	1496(3)	1337(4)	336(10)					
12	50(12)	894(15)	2784(14)	330(4)	C(4M)	5277(5)	1127(3)	592(4)	373(11)					

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SYNTHESIS AND CRYSTAL STRUCTURE

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Bond	<i>d</i> , Å	Bond	d, Å Bond				
		Ι			•		
Au(1)–C(2 <i>M</i>)	2.00(3)	Au(2)–C(4 <i>M</i>)	2.016(18)	C(1)–C(2)	1.52(2)		
Au(1)–C(1 <i>M</i>)	2.03(2)	Au(2)–O(3)	2.151(16)	O(3)–C(3)	1.22(3)		
Au(1)–O(4)	2.150(14)	Au(2)–O(2)	2.165(12)	O(4)–C(3)	1.28(3)		
Au(1)–O(1)	2.173(15)	O(1)–C(1)	1.25(2)	C(3)–C(4)	1.54(3)		
Au(2)–C(3 <i>M</i>)	1.982(17)	O(2)–C(1)	1.25(2)	25(2)			
	I	" II		11	1		
Au(1)–C(2 <i>M</i>)	2.015(5)	Au(2)–C(3 <i>M</i>)	2.030(4)	C(1)–C(2)	1.538(6)		
Au(1)–C(1 <i>M</i>)	2.018(4)	Au(2)–O(4)	2.126(3)	O(3)–C(3)	1.246(5)		
Au(1)–O(3)	2.120(3)	Au(2)–O(2)	2.135(3)	O(4)–C(3)	1.270(5)		
Au(1)–O(1)	2.131(3)	O(1)–C(1)	1.249(5)	C(3)–C(4)	1.534(6)		
Au(2)–C(4 <i>M</i>)	2.017(4)	O(2)–C(1)	1.242(5)				
	I	III		11	1		
Au(1)–C(1 <i>M</i>)	2.021(3)	Au(2)–O(2)	2.1301(16)	C(1)–C(2)	1.502(3)		
Au(1)–O(1)	2.1400(16)	O(1)–C(1)	1.251(2)				
Au(2)–C(2 <i>M</i>)	2.017(3)	O(2)–C(1)	1.251(2)				
Angle	ω, deg	Angle	w, deg	Angle	ω, deg		
	I	I		.11			
C(2 <i>M</i>)Au(1)C(1 <i>M</i>)	88.2(12)	C(4M)Au(2)O(3)	178.1(7)	O(1)C(1)C(2)	114.3(17)		
C(2 <i>M</i>)Au(1)O(4)	90.2(10)	C(3M)Au(2)O(2)	175.6(7)	C(3)O(3)Au(2)	125.3(13)		
C(1 <i>M</i>)Au(1)O(4)	176.9(8)	C(4 <i>M</i>)Au(2)O(2)	92.9(8)	C(3)O(4)Au(1)	126.1(12)		
C(2 <i>M</i>)Au(1)O(1)	176.8(8)	O(3)Au(2)O(2)	88.2(6)	O(3)C(3)O(4)	129.5(17)		
C(1 <i>M</i>)Au(1)O(1)	93.1(10)	C(1)O(1)Au(1)	124.0(12)	O(3)C(3)C(4)	117(2)		
O(4)Au(1)O(1)	88.4(6)	C(1)O(2)Au(2)	126.6(10)	O(4)C(3)C(4)	113.4(19)		
C(3 <i>M</i>)Au(2)C(4 <i>M</i>)	87.9(9)	O(2)C(1)O(1)	130.1(15)				
C(3 <i>M</i>)Au(2)O(3)	90.8(8)	O(2)C(1)C(2)	115.6(15)				
	I	II		11	Ι		
C(2 <i>M</i>)Au(1)C(1 <i>M</i>)	88.3(2)	C(3M)Au(2)O(4)	177.96(15)	O(1)C(1)C(2)	116.0(4)		
C(2 <i>M</i>)Au(1)O(3)	90.88(19)	C(4 <i>M</i>)Au(2)O(2)	174.24(15)	C(3)O(3)Au(1)	126.6(3)		
C(1 <i>M</i>)Au(1)O(3)	178.88(19)	C(3 <i>M</i>)Au(2)O(2)	91.15(17)	C(3)O(4)Au(2)	127.5(3)		
C(2 <i>M</i>)Au(1)O(1)	172.34(16)	O(4)Au(2)O(2)	90.07(13)	O(3)C(3)O(4)	126.0(4)		
C(1 <i>M</i>)Au(1)O(1)	92.06(19)	C(1)O(1)Au(1)	128.3(3)	O(3)C(3)C(4)	116.7(4)		
O(3)Au(1)O(1)	88.83(15)	C(1)O(2)Au(2)	126.1(3)	O(4)C(3)C(4) 117.			
C(4 <i>M</i>)Au(2)C(3 <i>M</i>)	87.5(2)	O(2)C(1)O(1)	125.9(4)				
C(4 <i>M</i>)Au(2)O(4)	91.09(17)	O(2)C(1)C(2)	118.1(4)				
	I	III	I	11	I		
C(1 <i>M</i>)#Au(1)C(1 <i>M</i>)	87.5(2)	$\left\ C(2M) \# Au(2)C(2M) \right\ $	88.4(3)	C(1)O(1)Au(1)	130.18(14)		
C(1 <i>M</i>)#Au(1)O(1)	176.35(9)	C(2 <i>M</i>)#Au(2)O(2)	178.81(12)	C(1)O(2)Au(2)	123.77(14)		
C(1 <i>M</i>)Au(1)O(1)	91.11(13)	C(2 <i>M</i>)Au(2)O(2)	92.19(15)	O(2)C(1)O(1)	126.27(19)		
O(1)Au(1)O(1)#	90.09(12)	O(2)Au(2)O(2)#	87.22(11)				

Table 4. The main bond lengths and bond angles in compounds I–III*

* The symmetry transformations for the equivalent atoms in **III**: # x, -y + 1/2, z.

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Fig. 1. The structure of the molecule of (a) $[Me_2Au(Tfa)]_2$ (I), (b) $[Me_2Au(Piv)]_2$ (II), and (c) $[Me_2Au(OBz)]_2$ (III) with atomic numbering.

 -30° C; the lowering of the temperature to -70° C did not affect the [Me₂AuI]₂ yield. The analogous lowering of the temperature from -23° C to -70° C performed in [13] did not change the product yield either; however, the yield decreased sharply to 15% when the reaction was run at -10° C. An increase in the molar amount of MeLi from 3 to 6 relative to KAuCl₄ did not produce substantial effect on the dimehtylgold(III) iodide yield. Upon variation of the solvent ratio, the best results were attained at the 1.75 : 1 ratio of hexane and ether. When the reaction was performed for more than one hour, the yield of [Me₂AuI]₂ decreased. Thus, we suggested and optimized the procedure of the dimethylgold(III) iodide synthesis with 60% yield. The results close to our data were obtained by the authors of [16].

The synthesis of **I–III** was based on the method [3], where complex **IV** was prepared from silver acetate and dimethylgold(III) iodide. In the case of dimethylgold(III) carboxylates, the reaction time was reduced to 1 h and the flow of argon was passed through the reaction mixture. The procedure of the synthesis we developed makes it possible to obtain dimethylgold(III) carboxylates in high yields (Table 1).

The IR spectra of compounds I–III contain characteristic stretching vibrations $v(C-H)(Au-CH_3)$ in a range of 2800–3000 cm⁻¹. The analogous vibrations are observed for dimethylgold(III) acetate at 2850–

	T _{mp} , °C	Crystal system	ρ(calcd.), g/cm ³	<i>V/Z</i> , Å ³	<i>d</i> , Å			
Complex					Au…Au in the dimer	Au…Au between the dimmers	Au–O	Au–C(Me)
IV*	95–96	Monoclinic	2.917	325.70	2.989	3.637	2.125	2.023
I	102–103	Monoclinic	2.959	381.60	3.080	3.294; 3.462	2.160	2.007
II	75–76	Monoclinic	2.224	490.09	3.028	3.479	2.128	2.020
III	185–187	Rhombic	2.401	481.64	2.984	3.468	2.135	2.019

Table 5. The crystallographic characteristics and average geometric parameters of dimethylgold(III) carboxylates I-IV

* The data of [3].



Fig. 2. The fragment of the chain of the molecules in the crystal of (a) I, (b) II, and (c) III.

2960 cm⁻¹ [3]. The bending vibrations of the Au–CH₃ bond are observed in the region 1210–1240 cm⁻¹ (for **IV**, 1216–1235 cm⁻¹ [3]). The bending vibrations of the phenyl substituents C–C–C in complex **III** and the stretching vibrations of the C–F bond in complex **I** appear in a range of 1000–1200 cm⁻¹. The intense vibrations v(C–O) typical of all the chelates are observed in the frequency interval 1360–1700 cm⁻¹. For dimethylgold acetate **IV**, the stretching vibrations of the C–O bond appear at 1420–1580 cm⁻¹ [3]. In the region 400–900 cm⁻¹, the largest contribution is produced by the vibrations of the bonds Au–O, C–R (R = CF₃, *tert*-Bu, Ph), the deformation of the chelate ring and the ligand substituents.

The ¹H NMR spectra of compounds **I–III** contain typical singlet signal due the protons of the methyl group $\delta_{\rm H}({\rm Au-CH_3})$ in the region 1.1–1.4 ppm. In the spectrum of compound **I**, the singlet $\delta_{\rm H}({\rm Au-CH_3})$ is observed in a lower field (1.37 ppm) as compared to the other carboxylates. The value $\delta_{H}(Au-CH_{3})$ in the ¹H NMR spectrum of complex **II** (1.10 ppm) is close to that of the analogous shift for **IV** (1.13 ppm) [3].

The molecular structure of the complexes under consideration consists of neutral binuclear molecules of $[(CH_3)_2Au(OOCR)]_2$ (R = CF₃ (I), C(CH₃)₃ (II), and C_6H_5 (III)), whose structures are shown in Fig. 1. Some characteristics of the novel complexes I-III are compared with similar characteristics of the previously studied complex IV [3] in Table 5. The square coordination of the Au atom in I-IV involves two C atoms of the methyl groups and two O atoms of two carboxylate groups. The difference between the average $Au-CH_3$ and Au-O distances for complexes I-IV does not exceed 0.016 and 0.035 Å, respectively. The bond angles at the Au atoms deviate from 90° by no more than 3.1° . The coordination squares of Au(1) and Au(2) in the dimers are not parallel, and the angles between the normals to their planes are 34.5° , 36.9° , and 31.8° for compounds I, II, III, respectively. In the binuclear molecules, the bridging carboxylate groups form two five-membered chelate rings with the angle between the normals to their plane being on the average $\sim 90.8^{\circ}$. The lengths of the analogous bonds O-C and C-C_{Me} in the carboxylate groups of compounds I-III are almost equal, their average values being 1.25 and 1.52 Å, respectively. The average bond lengths in the substituents are: C-F 1.30 Å in I, C-C 1.533 Å in II and 1.389 Å in III. The planes of the phenyl radicals in complex III make an angle of 9.4° with the planes of the metal rings.

In the structures of compounds I–III, the dimeric molecules are packed into infinite unidimensional chains (Fig. 2). The Au…Au distances between the molecules in the chains of II and III are equal (~3.47 Å), while in compound I, this distance is somewhat shorter and is equal to 3.29 Å. Thus, the coordination of gold is completed to the square bipyramid with the second Au atom in the dimer and with the H(Me) atoms of the neighboring complexes (Au…H ~3.3 Å) for compounds II and III and with the Au atom of the neighboring molecule of the chain in complex I. In all the three compounds, the molecules form zigzag chains, the average AuAuAu angles being ~156° in I, 162° in II, and 173° in III.

The general packing of complexes in crystals **I–III** is shown in Fig. 3. The dimeric chains are linked by the van der Waals interactions, the shortest distances H···H and F···F being 2.3 and 2.8 Å, respectively. The Au···Au distances between the chains exceed 7.2 Å.

ACKNOWLEDGMENTS

The authors are grateful to A. V. Alekseev for performing the powder X-ray diffraction experiment and



Fig. 3. The molecular packing in the crystal of (a) I, (b) II, and (c) III.

to A. I. Smolentsev for performing the X-ray diffraction analysis. This work was supported by NPF OOO "TECHNOLET-ZOLOTO" in the framework of the State Contract no. 3631p/6147 with the Foundation for assistance to small business in the area of science and technology.

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