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Volatile Dimethylgold(III) β-Iminovinylthionates: Synthesis, Structure, and Properties

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Abstract—Volatile dimethylgold(III) β-iminovinylthionates, $(CH_3)_2Au(CH_3CSCHC(NH)CH_3)$ (**I**) and $(CH_3)_2Au(CF_3CSCHC(NH)CH_3)$ (**II**), were studied. For complexes **I** and **II**, the synthesis is described and data from elemental analysis, IR and UV/Vis spectra, DTA, and X-ray diffraction are given. The structures of **I** and **II** are composed of monomeric complexes combined into polymeric stack-type associates. The distorted square environment of gold is formed by sulfur and nitrogen atoms of the chelating ligand and two carbon atoms of the methyl groups. For complex **I**, the average Au–S bond length is 2.260 Å, the Au–N bond length is 2.137 Å, and the chelate angle SAuN is 94.1°; for II, these values are 2.355 Å, 2.088 Å, and 93.7°, respectively.

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Dimethylgold(III) complexes with β-diketones and their derivatives are among the few known volatile gold(III) compounds used in chemical vapor deposition (CVD) processes to produce gold coatings [1]. These compounds are known to have a broad range of volatility and thermal stability in the condensed and gaseous states depending on the terminal substituents and on the type of donor atoms in the ligand. The dimethylgold(III) complexes with chelating ligands $(CH_3)_2AuL$, where L is β-diketone, β-aminovinyl ketone, β-mono- or β–dithioketone, β-aminovinylthione, and other, are convenient model systems for studying the composition–structure—property relationships for this practically valuable class of volatile compounds. These studies promote the development of targeted synthesis of most appropriate precursors for CVD processes to produce gold coatings.

Previously, we studied the conditions of synthesis, spectral characteristics, volatility, and thermal properties of dimethylgold(III) complexes based on β-diketones, β-iminoketones, and β-thioketones [2–4]. The structures of some of these complexes have been studied previously [5]. As a continuation of the systematic research into this class of compound, we studied the dimethylgold complexes with N,S-analogs of β-diketones, which had not been reported previously.

This communication reports the synthesis and study of two volatile Au(III) β-vinylthionate complexes: (4-iminopent-3-ene-2-thionate)dimethylgold $(CH_3)_2Au(CH_3–CS–CH–C(NH)–CH_3)$ (**I**) and (1,1,1-trifluoro-4-imino-pent-3-ene-2-thionate)dimethylgold $(CH_3)_2Au(CF_3–CS–CH–C(NH)–CH_3)$ (**II**). Data from IR and UV/Vis spectra and DTA measurements for these complexes are presented.

EXPERIMENTAL

The volatile dimethylgold complexes were synthesized using 4-aminopent-3-ene-2-thione and 1,1,1-trifluoro-4-aminopent-3-ene-2-thione, prepared by sulfonation of appropriate β-aminovinyl ketones. 2,4-Bis(4-methoxyphenyl)-2,4-dithioxo-P^v,P^v-1,3,2,4-dithiophosphetane, prepared by a known procedure [6], was used as the sulfonating agent. The pure state of the β-aminovinylthiones thus formed was confirmed by comparing thir IR and ^{1}H NMR spectra with the reported spectra [7, 8].

The synthesis of I. A solution of the complex $[(CH_3)_2AuI]_2$ (1 g, 1.4 mmol) in benzene (50 ml) was mixed with a solution of 4-aminopent-3-ene-2-thione (0.32 g, 2.8 mmol) in benzene (20 ml), and KOH (0.15 g, 2.8 mmol) in ethanol (30 ml) was added. The reaction mixture was stirred at room temperature until the solution color changed from red to light yellow. After evaporation of the solvent, the residue was extracted with hexane. The product isolated from hexane was chromatographed on a column with silica gel using a benzene–hexane mixture (1 : 4) as the eluent. The compound was additionally purified by vacuum sublimation at $P = 10^{-2}$ mm Hg and $T = 180°C$. Yield 0.96 g (65%), mp = 83–85°C.

For $C_7H_{14}AuNS$

anal. calcd. %:	C, 24.63;	H, 4.11;	N, 4.10;	S, 9.38.
Found (%):	C, 24.43;	H, 3.83;	N, 4.24;	S, 9.12.

IR (ν, cm^{-1}): 3300 m ν(N–H); 2983, 2930, 1591, 1513, 1432, 1338, 1228, 1200, 1174, 1117, 1035, 836, 800 s ν(C = S); 718, 675, 550 w ν(Au–C), 510, 490.

UV/Vis ($\nu_{max} \times 10^{-3}$, cm^{-1} (log ε)): 38.2 (4.25), 37.2 (4.16), 27.0 (4.63).

The synthesis of II. A solution of the complex $[(CH_3)_2AuI]_2$ (1 g, 1.4 mmol) in benzene (50 ml) and a solution of 1,1,1-trifluoro-4-aminopent-3-ene-2-thione (0.47 g, 2.8 mmol) in benzene (20 ml) were mixed, and KOH (0.15 g, 2.8 mmol) in ethanol (30 ml) was added. The subsequent reaction and product isolation and sublimation were carried out as described for complex **I**. Yield 0.88 g (80%), mp = 76–78°C.

For $C_7H_{11}AuF_3NS$

anal. calcd. %:	C, 21.27;	H, 2.78;	N, 3.54;	S, 8.10.
Found (%):	C, 21.52;	H, 2.94;	N, 3.33;	S, 8.35.

IR (ν, cm^{-1}): 3318 m ν(N–H), 2980, 2914, 1628, 1544, 1420, 1378, 1354, 1260, 1242, 1183, 1160, 1132, 1042, 1008, 878, 803 s ν(C=S); 744, 720, 645, 550 w ν(Au–C), 500.

UV/Vis ($\nu_{max} \times 10^{-3}$, cm^{-1} (log ε)): 38.2(4.29), 37.2 (4.18), 26.2 (4.55).

The IR spectra of complexes **I** and **II** in the 400–4000 cm^{-1} range were recorded on a Scimitar FTS-2000 spectrometer (KBr pellets). The UV/Vis spectra (20000–45000 cm^{-1}) were measured on a Specord M40 spectrophotometer (reference grade heptane as the solvent, a 0.2 cm cell, $c = 1 \times 10^{-4}$ mol/l). DTA was carried out in a helium flow using a Setaram microanalyzer (heating rate 5 deg/min, ΔT = ±1°C, gas flow 110–120 ml/min, 10 mg sample, standard crucible).

X-Ray Diffraction. The single crystals of complexes **I** and **II** were grown from heptane solutions at –2°C. The unit cell parameters and the experimental intensities for crystal structure solution were measured at –123(2)°C on a Bruker-Nonius X8Apex four-circle automated diffractometer (CCD xy-detector, MoK_α radiation, λ = 0.71073 Å, graphite monochromator). The structures of **I** and **II** were solved by the direct method and refined in the anisotropic approximation. The H atoms were specified geometrically and included in the refinement in the isotropic approximation together with non-hydrogen atoms.

The crystal data or **I** and **II** and X-ray experiment details are summarized in Table 1 and selected interatomic distances and bond angles are given in Table 2. All calculations were carried out using SHELX-97 software [9].

Table 1. Crystal data and X-ray experiment details for complexes **I** and **II**

Parameters	Value	
	I	II
M	341.22	395.19
Space group	$Ima2$	$P2_1/n$
a, Å	13.993(3)	15.0411(13)
b, Å	11.354(2)	8.1461(6)
c, Å	6.0545(10)	17.8320(15)
β, deg	90	104.311(2)
V, $Å^3$	961.9(3)	2117.1(3)
Z	4	8
ρ(calcd), g/cm^3	2.335	2.480
μ_{Mo}, mm^{-1}	15.444	14.092
$F(000)$	620	1456
Scan range θ, deg	3.5–28.38	1.59–25.35
Index range	$-18 \le h \le 18$, $-15 \le k \le 15$, $-4 \le l \le 7$	$-18 \le h \le 18$, $-4 \le k \le 9$, $-21 \le l \le 21$
I_{hkl} measured	3639	10384
I_{hkl} independent	950 (R_{int} = 0.0242)	3862 (R_{int} = 0.0485)
$I_{hkl} > 2\sigma(I)$	906	2678
GOOF for F^2_{hkl}	1.116	0.975
R-factor ($I > 2\sigma(I)$)	$R_1 = 0.0163$, $wR_2 = 0.0380$	$R_1 = 0.0552$, $wR_2 = 0.1322$
R-factor (all reflections)	$R_1 = 0.0182$, $wR_2 = 0.0387$	$R_1 = 0.0793$, $wR_2 = 0.1452$
Residual electron density (max/min), e $Å^{-3}$	1.381/–0.921	4.315/–4.048

Table 2. Selected interatomic distances and bond angles in structures **I** and **II***

Bond	d, Å	Angle	ω, deg
		I	
Au(1)–C(1M)	2.051(6)	C(1M)Au(1)C(1M)$^{\#1}$	88.9(4)
Au(1)–N(1)	2.137(12)	C(1M)Au(1)N(1)$^{\#1}$	174.9(4)
Au(1)–S(1)	2.260(4)	N(1)Au(1)S(1)$^{\#1}$	94.1(4)
S(1)–C(1)	1.745(7)	C(1M)Au(1)S(1)	80.8(2)
N(1)–C(1)	1.296(13)	C(1)S(1)Au(1)	105.5(3)
C(1)–C(2)	1.383(8)	C(1)N(1)Au(1)	136.3(8)
C(1–C(3)	1.531(9)	N(1)C(1)C(2)	119.0(8)
		N(1)C(1)C(3)	125.0(7)
		C(2)C(1)C(3)	115.9(6)
		C(2)C(1)S(1)	134.4(6)
		C(3)C(1)S(1)	109.6(4)
		C(1)C(2)C(1)$^{\#1}$	130.7(9)
		II	
Au(1)–C(17)	2.030(12)	C(17)Au(1)C(18)	88.0(5)
Au(1)–C(18)	2.079(12)	C(17)Au(1)N(11)	89.0(4)
Au(1)–N(11))	2.080(9)	C(18)Au(1)N(11)	177.0(4)
Au(1)–S(11)	2.358(3)	C(17)Au(1)S(11)	177.2(4)
Au(2)–C(28)	2.035(11)	C(18)Au(1)S(11)	89.3(4)
Au(2)–C(27)	2.079(12)	N(11)Au(1)S(11)	93.7(2)
Au(2)–N(21)	2.097(8)	C(28)Au(2)C(27)	86.1(5)
Au(2–S(21)	2.352(3)	C(28)Au(2)N(21)	177.0(4)
S(11–C(15)	1.716(12)	C(27)Au(2)N(21)	90.9(5)
S(21)–C(25)	1.724(12)	C(28)Au(2)S(21)	89.3(4)
N(11C(13)	1.295(13)	N(11)C(13)C(14)	124.8(11)
C(13)–C(14)	1.412(16)	C(15)C(14)C(13)	130.9(11)
C(15)–C(16)	1.491(16)	C(14)C(15)S(11)	130.5(10)
		N(21)C(23)C(24)	124.7(10)
		C(25)C(24)C(23)	130.6(11)
		C(24)C(25)S(21)	131.0(10)

* Symmetric transformations of equivalent atoms: $^{\#1}$ $-x + 1, -y, -z + 1$.

The atom coordinates and other parameters of **I** and **II** are deposited with the Cambridge Crystallographic Data Collection (no. 678695 for **I** and no 678657 for **II**); see deposit@ccde.cam.ac.uk.

RESULTS AND DISCUSSION

Compounds **I** and **II** are slightly yellow-colored transparent plates stable in the light and in air and readily soluble in common organic solvents.

On heating in inert atmosphere, complexes **I** and **II** behave similarly. The DTA curves show melting and decomposition effects. Between these effects, the curve smoothly declines indicating sublimation of the compound on heating; this is more typical of the fluorinated complex **II**. According to TGA data, sublimation of complex **I** under recording conditions starts at 89°C, the loss of sample mass during sublimation before decomposition is 73.8%, and decomposition starts at 168°C. Complex **II** is more volatile, its sublimation starts at 65°C, the loss of sample mass during sublimation before decomposition is 98%, and decomposition starts at 162°C. Comparison of the thermal stabilities of β-iminovinylthionate complexes **I** and **II** with those of similar dimethylgold(III) complexes with β-diketones, β-iminoketones, and β-thioketones reported in the literature [3] has shown that complexes with N,S-derivatives of β-diketones are more stable than complexes with O,O- or S,O-donor atoms in the chelate unit but are less stable than O,N-analogs.

The molecular structure of **I** is composed of neutral monomers. The molecule lies in plane *m*; therefore, the S and N atoms of the chelate ring are disordered over two equally probable positions. The structure of complex **I** with atom numbering is presented in Fig. 1. The distorted square coordination of gold is formed by sulfur and nitrogen atoms of the chelating ligand and by two carbon atoms of the methyl groups. The Au–S bond length is 2.260 Å, the Au–N bond length is 2.137 Å, and the chelate angle SAuN is 94.1°. The Au–C_{Me} distance and the CAuC bond angle in **I** (2.051 Å and 87°, respectively) are consistent with the data for β-diketonate derivatives of dimethylgold(III) [5]. The bond lengths in the organic ligand are as follows: S–C, 1.745 Å; N–C, 1.296 C–C_γ 1.383 Å. Molecule **I**, except for the hydrogen atoms of the methyl groups, is planar to an accuracy ±0.02 Å, the folding angle of the chelate ring along the S···N line being only 0.8°. The square coordination of the gold(III) atom is supplemented on one side by contacts with two H atoms of the methyl groups of the neighboring complex (Au···H 3.45 Å).

The general molecular packing in the crystal of **I** along the *z* axis is shown in Fig. 2a. In the structure, one can distinguish layers of complexes perpendicular to *x* axis with the interplanar spacing $d(200) = 7.0$ Å. The orientation and bonding of complexes in the layer is shown in Fig. 2b. The layers are combined by intermo-

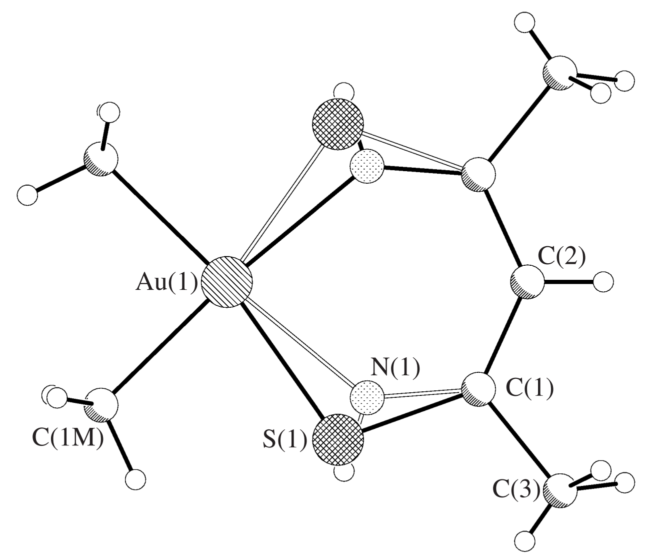

Fig. 1. Structure of complex **I**.

lecular H-bonds N–H···S (H···S ≥ 2.96 Å). Molecule **I** is surrounded by eight similar molecules (Au···Au 5.323–7.600 Å).

In the molecular structure of **II**, two crystallographically independent gold complexes have similar structures (Fig. 3). The distorted square environment of gold includes the sulfur and nitrogen atoms of the chelating ligand and two carbon atoms of the methyl groups. The average bond lengths are as follows: Au–S, 2.355 Å; Au–N, 2.088 Å; the average SAuN chelating angle is 93.7°; the average Au–C distance is 2.056 Å and the CAuC bond angle is 87°. The average bond lengths in the ligand are as follows: S–C, 1.72 Å; N–C, 1.34 Å. The C–C_γ bonds on the side of the fluorinated substituent are on average 0.07 Å shorter than those on the CH_3 group side. The average C–F bond length is 1.34 Å. Molecule **II**, except for the fluorine and hydrogen atoms of the ligand terminal groups, is planar to an accuracy ±0.02 Å, the folding angles of the chelate rings along the S···N lines being not greater than 5.4°. The C(14)C(15)C(16)F(13) and C(24)C(25)C(26)F(22) torsion angles are ~24°. The (4 + 2) gold(III) coordination in **II** is completed by axial contacts with two H atoms of the neighboring complex (Au···H 3.26 and 3.38 Å). The general molecular packing in the crystal of **II** along the *y* axis is shown in Fig. 4. The complexes are combined by H-bonds C–H···S (H···S ~2.9 Å). In the fluorinated complex **II**, the Au–S distance is 0.09 Å longer and the Au–N distance is 0.05 Å shorter than those in the nonfluorinated complex **I**, i.e., one can suggest that the CF_3 group present in the ligand weakens the Au–S bond.

Thus, we studied the structures of two volatile dimethylgold(III) β-iminovinylthionates. The obtained

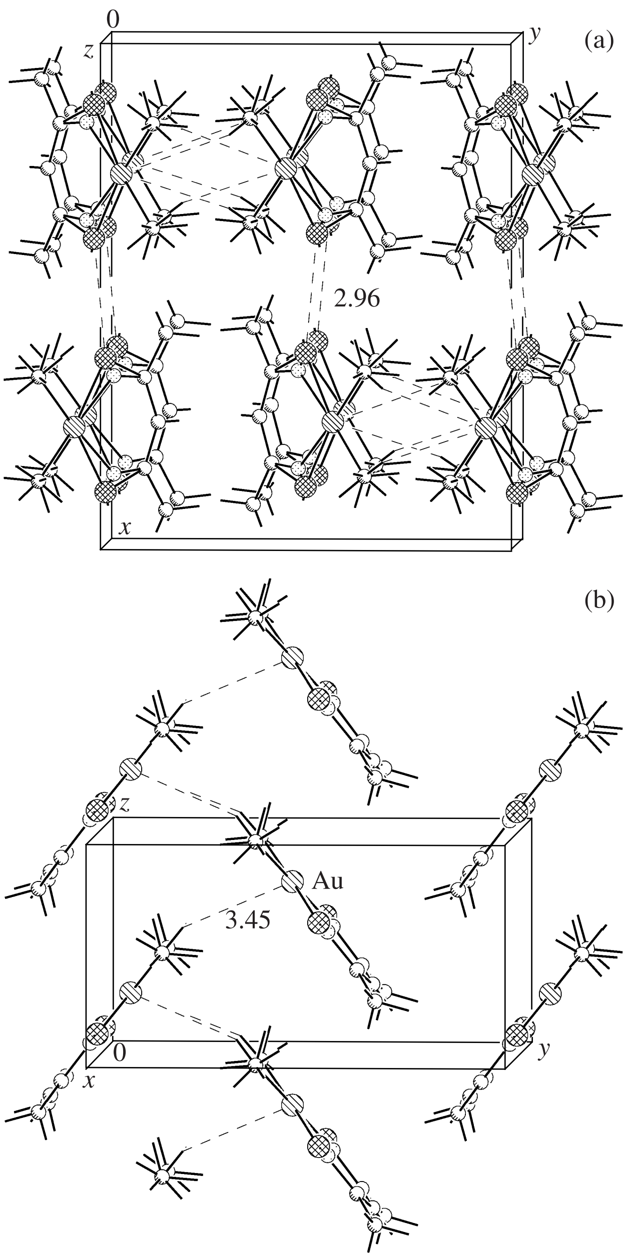

Fig. 2. (a) Projection of structure **I** along the *z* axis; (b) orientation and bonding of complexes in the layer.

structural data can serve as the basis for calculation of the intermolecular interaction in the crystals of these compounds containing N,S-donor atoms in the coordination unit in order to estimate their volatility against the series of related dimethylgold(III) complexes with (O,O)-, (O,S)-, and (O,N)-type chelate units that we studied previously. The DTA study has shown that complex **II** based on the fluorinated ligand is fairly volatile and thermally stable and can be recommended for CVD applications.

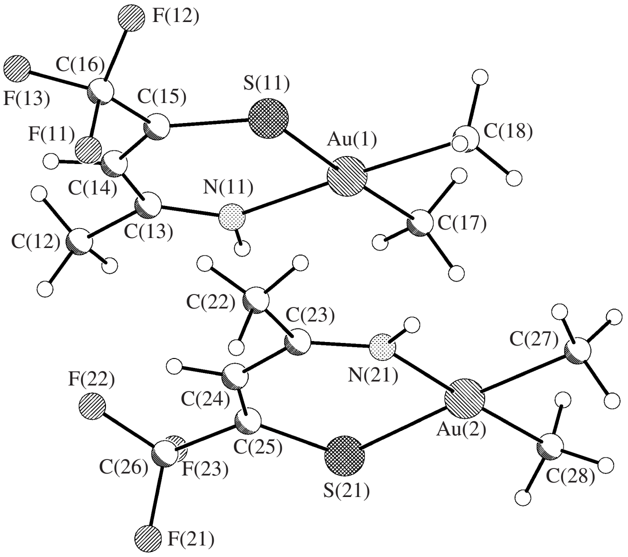

Fig. 3. Structure of independent complexes in structure **II**.

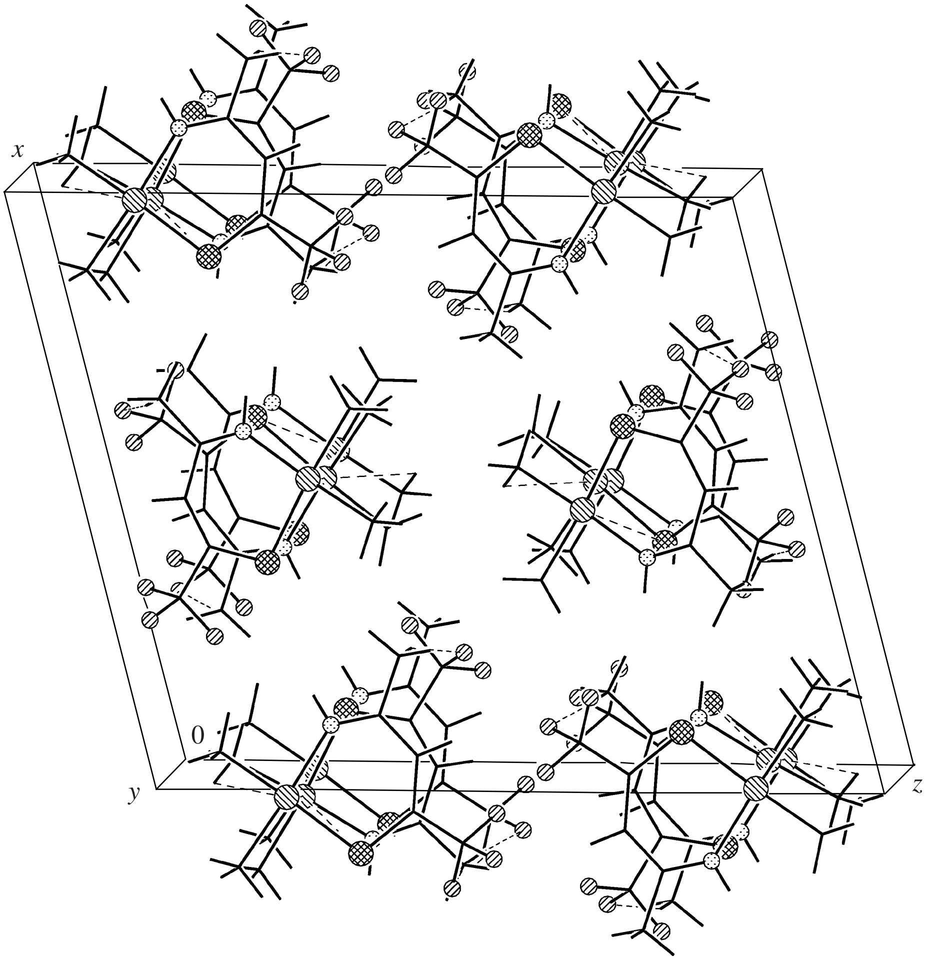

Fig. 4. Packing of molecules in structure **II** along the *y* axis.

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