# Binding Forms of Gold(III) from Solutions by Cadmium Diethyl Dithiocarbamate: Thermal Behavior and Role of Secondary Interactions in the Supramolecular Self-Assembly of Polymeric Complexes ( $[Au{S_2CN(C_2H_5)_2}_2][AuCl_4]$ )<sub>n</sub> and $[Au{S_2CN(C_2H_5)_2}Cl_2]_n$

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Abstract—The chemisorption interaction between the binuclear cadmium diethyl dithiocarbamate (EDtc),  $[Cd_2\{S_2CN(C_2H_5)_2\}_4]$ , (chemisorbent I) and AuCl<sub>3</sub> solutions in 2 M HCl results in the formation of polymeric gold(III) complexes: ( $[Au\{S_2CN(C_2H_5)_2\}_2][AuCl_4]$ )<sub>n</sub> (II) and  $[Au\{S_2CN(C_2H_5)_2\}Cl_2]_n$  (III) with the same Au : EDtc : Cl ratio (1 : 1 : 2). The alternating centrosymmetric cations and anions of complex II are structurally self-assembled to form linear polymeric chains: the gold atom in  $[Au\{S_2CN(C_2H_5)_2\}_2]^+$  forms secondary Au(1)…Cl(1) bonds (3.7784 Å) with two neighboring  $[AuCl_4]^-$  anions. This binding is additionally strengthened by secondary S(1)…Cl(1) interactions (3.4993 Å). The mixed-ligand complex III comprises two structurally non-equivalent molecules  $[Au\{S_2CN(C_2H_5)_2\}Cl_2]: A - Au(1)$  and B - Au(2), each being in contact with two nearest neighbors through pairs of unsymmetrical secondary bonds: Au(1)…S(1)<sup>a/b</sup> 3.4361/3.6329; and Au(2)…S(4)<sup>c/d</sup> 3.4340/3.6398 Å. At the supramolecular level, this gives rise to independent zigzag-like polymeric chains, (…A…A…A…)<sub>n</sub> and (…B…B…B…)<sub>n</sub> along which antiparallel isomeric molecules of III alternate. The chemisorption capacity of cadmium diethyl dithiocarbamate calculated from the gold (III) binding reaction is 963.2 mg of gold per 1 g of the sorbent. The recovery conditions for the bound gold were elucidated by simultaneous thermal analysis of II and III. The DSC curves reflect different sets of heat effects, because thermolysis occurs for complex molecules (III) or for cations and anions (II). Nevertheless, the patterns of experimental TG curves are similar despite different structures of the complexes. The final product of thermal transformations is reduced gold.

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# **INTRODUCTION**

Dithiocarbamate cadmium(II) complexes [1-4] and adducts they form with organic N-donor bases [5-9] are of interest as precursors of film and nanocrystalline cadmium sulfides. When searching for antidotes against cadmium intoxication, the ability of dialkyl dithiocarbamates to bind cadmium into stable

compounds appears an important feature [10-12]. One more important aspect of the possible practical application of cadmium dithiocarbamates is due to their ability to efficiently collect gold from acidic solutions [4, 14–17]. As individual gold-binding species, a variety of polynuclear and heteropolynuclear complexes with highly intricate supramolecular structures were preparatively isolated. Gold complexes with dithio ligands, both dithiocarbamates and dithiophosphates, can behave as highly efficient anticancer agents [18], sensors for volatile chemicals [19] or luminophores [20-22].

Here we considered the reaction of freshly precipitated cadmium diethyl dithiocarbamate (EDtc)  $[Cd_2{S_2CN(C_2H_5)_2}_4]$  (chemisorbent I) with a solution of AuCl<sub>3</sub> in 2 M HCl and elucidated the sorption capacity of this material. The heterogeneous gold(III)-binding reaction includes chemisorption and ion exchange. Two individual gold species with the same Au : EDtc : Cl ratio (1 : 1 : 2) were preparatively isolated, namely, (i) a polymeric gold(III) complex of ionic structure ([Au{S\_2CN(C\_2H\_5)\_2}\_2][AuCl\_4])<sub>n</sub> (II) and (ii) a polymeric mixed-ligand complex [Au{S\_2CN(C\_2H\_5)\_2}Cl\_2]<sub>n</sub> (III). The molecular and supramolecular structures of II and III were estab-

<sup>&</sup>lt;sup>1</sup> Despite high toxicity of cadmium, a metalloenzyme in which cadmium linked to two (or more) thiolate groups of amino acids acts as the active site was isolated from a marine diatom [13].

lished from X-ray diffraction data. At the supramolecular level, the obtained compounds self-assemble into polymeric chains through Au…S, Au…Cl, and Cl…S secondary bonds. The recovery conditions of the bound gold and the thermal behavior of complexes II and III were studied by simultaneous thermal analysis (STA).

### **EXPERIMENTAL**

Commercial sodium diethyl dithiocarbamate trihydrate (Sigma-Aldrich) was used as received. The initial binuclear complex, chemisorbent I, was prepared according to reported data [23, 24]. The initial sodium salt and complex I were characterized using the <sup>13</sup>C MAS NMR data ( $\delta$ , ppm): Na{S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>} ·  $3H_2O(1:2:2): 206.5(-S_2CN=); 48.6(-CH_2-); 13.2$  $[Cd_{2}{S_{2}CN(C_{2}H_{5})_{2}}_{4}]:$  $(-CH_3).$ 203.3(28)\*, 199.2(26)\* (1:1, -S<sub>2</sub>CN=); 53.1, 52.4, 51.4 (1:1:2, -CH<sub>2</sub>-); 13.6, 12.9, 12.7, 12.4 (1 : 1 : 1 : 1, -CH<sub>3</sub>). \* Asymmetric  ${}^{13}C-{}^{14}N$  doublets [25, 26], in Hz.

The sorption of gold(III) was conducted in the static mode. 10 mL portions of a solution of  $H[AuCl_{4}]$ containing 108.40 mg of gold were added to 100-mg portions of sorbent I and the mixtures were magnetically stirred for 1-90 min. After certain periods of time, 0.1 mL samples were taken from the solutions to determine the residual concentration of gold. The degree of sorption (S, %) was calculated by the relation

$$S = [(c - c_{\rm r})/c] \times 100,$$

where *c* is the initial and  $c_r$  is the residual contents of gold in the solution. The amount of adsorbed gold(III) is determined by this difference. The gold content in the solutions was found on a 1st class Hitachi atomic absorption spectrometer (design type 180-50).

Synthesis of II and III.<sup>2</sup> Polymeric bis(N,N-diethyldithiocarbamato-S, S')gold(III) tetrachloroaurate(III) (II) and dichloro(N,N-diethyldithiocarbamato-S,S')gold(III) (III) were synthesized by the reaction of freshly precipitated cadmium diethyl dithiocarbamate with solutions of AuCl<sub>3</sub> in 2 M HCl. The heterogeneous reaction can be represented as follows:

$$[Cd_{2}\{S_{2}CN(C_{2}H_{5})_{2}\}_{4}] + 4H[AuCl_{4}]$$
  
= [Au{S\_{2}CN(C\_{2}H\_{5})\_{2}}\_{2}][AuCl\_{4}]  
+ 2[Au{S\_{2}CN(C\_{2}H\_{5})\_{2}}Cl\_{2}] + 2CdCl\_{2} + 4HCl.

A solution of AuCl<sub>3</sub> in 2 M HCl (20 mL) containing 216.8 mL of gold was added to 200 mg of freshly precipitated cadmium diethyl dithiocarbamate and the mixture was stirred for 1.5 h. The resulting yellow-

orange precipitate was filtered off, washed with water, and dried on the filter. Transparent yellow prismatic (II) and needle (III) crystals of the complexes for X-ray diffraction were obtained simultaneously from methanol. <sup>13</sup>C MAS NMR (δ, ppm): II, 188.8  $(-S_2CN=)$ ; 50.6  $(-CH_2-)$ ; 17.7, 14.8  $(1:1, -CH_3)$ ; III, 195.4 (32),\* 195.0 (1 : 1,  $-S_2CN=$ ); 52.5, 52.2  $(3:1, -CH_2-); 16.8, 15.9 (1:1, -CH_3). * Asymmet$ ric <sup>13</sup>C-<sup>14</sup>N doublet [25, 26], in Hz.

The <sup>13</sup>C MAS NMR spectra were recorded on a CMX-360 spectrometer (Agilent/Varian/Chemagnetics InfinityPlus) operating at 90.52 MHz with a superconducting magnet ( $B_0 = 8.46$  T) and Fourier transformation. The spectra were recorded with proton cross-polarization and  ${}^{13}C-{}^{1}H$  decoupling by radiofrequency field at the proton resonance frequency [30]. Samples weighing ~80 mg were placed in a 4.0 mm ZrO<sub>2</sub> ceramic rotor. The magic angle spinning was at 6100-6700(1) Hz; the number of acquisitions was 1000–1120; the duration of proton  $\pi/2$  pulses was  $3.3-4.9 \,\mu\text{s}$ ; <sup>1</sup>H-<sup>13</sup>C contact time was 2.5 ms; and pulse spacing was 3.0 s. The isotropic <sup>13</sup>C chemical shifts  $(\delta, ppm)$  are referred to one of components of external crystalline adamantane [31] ( $\delta = 38.48$  ppm relative to tetramethylsilane [32]).

Single crystal X-ray diffraction analysis of II and III was performed on a Bruker Kappa APEX II diffractometer (Mo $K_{\alpha}$  radiation,  $\lambda = 0.71073$  Å, graphite monochromator) at 170(2) K. The absorption corrections were applied by single crystal face indexes. The structure of II was determined by the direct method and refined by the least squares method (on  $F^2$ ) in the full-matrix anisotropic approximation for non-hydrogen atoms. The gold atom coordinates in III were determined from analysis of the function of interatomic vectors; the other non-hydrogen atoms were located from a series of difference electron density maps. A preliminary refinement of the resulting model of structure III gave a high *R*-factor of 0.13. Considering the similarity of periods a and c and based on analysis of  $F_0$  and  $F_c$  values, micro-twinning of the crystals of III was suggested. The introduction of the twin law for the second component with respect to the first one  $0 \ 0 \ 1/0 \ -1 \ 0/1 \ 0 \ 0$  resulted in a sharp decrease in the *R*-factor (down to 0.0140). The corrected mass coefficients of the twin components are 0.6270(3) and 0.3730(3). In both structures, the positions of hydrogen atoms were calculated geometrically and included in the refinement according to the "riding" model.

The data collection and editing and the refinement of the unit cell parameters were performed by the APEX2 [33] and SAINT [34] programs; the structure solution and refinement calculations were carried out by the SHELXTL/PC programs [35]. The atom coordinates, bond lengths, and bond angles are deposited with the Cambridge Crystallographic Data Centre (no. 942469 (II) and 942470 (III); deposit@ ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk). Selected crystallographic and structure refinement

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<sup>&</sup>lt;sup>2</sup> The preparation of complexes of this type reported in the literature [27-29] includes Au<sup>3+</sup> to Au<sup>+</sup> reduction, synthesis of gold(I) dibutyl dithiocarbamate followed by its halogenation with bromine or chlorine.

Denomination	Value			
Parameter	II	III		
Empirical formula	$C_{10}H_{20}N_2S_4Cl_4Au_2$	C <sub>5</sub> H <sub>10</sub> NS <sub>2</sub> Cl <sub>2</sub> Au		
M	832.25	416.13		
Crystal system	Monoclinic	Monoclinic		
Space group	$P2_1/n$	$P2_1/n$		
a, Å	7.85410(10)	17.2247(2)		
b, Å	12.3999(2)	7.05300(10)		
<i>c</i> , Å	10.9665(2)	17.2298(2)		
β, deg	99.7470(10)	97.6270(10)		
$V, Å^3$	1052.61(3)	2074.66(5)		
Ζ	2	8		
$\rho_{calcd}, g cm^3$	2.626	2.665		
$\mu$ , mm <sup>-1</sup>	14.822	15.040		
<i>F</i> (000)	768	1536		
Crystal size, mm	0.42  imes 0.29  imes 0.24	0.40  imes 0.07  imes 0.05		
Data collection range of $\theta$ , deg	2.50-30.65	1.19-32.32		
Ranges of reflection indices	$-11 \le h \le 11,$	$-25 \le h \le 25,$		
	$-17 \le k \le 17,$	$-10 \le k \le 10,$		
	$-15 \le l \le 15$	$-25 \le l \le 25$		
The number of measured reflections	26993	67860		
The number of independent reflections $(R_{int})$	3251 (0.0194)	7090 (0.0254)		
The number of reflections with $I > 2\sigma(I)$	2939	6815		
The number of refined parameters	106	204		
GOOF	1.094	1.062		
<i>R</i> -Factors on $F^2 > 2\sigma(F^2)$	$\begin{array}{c} R_1 = 0.0107 \\ wR_2 = 0.0266 \end{array}$			
<i>R</i> -Factors for all reflections	$R_1 = 0.0127$ $wR_2 = 0.0275$	$\begin{array}{c} R_1 = 0.0158 \\ wR_2 = 0.0327 \end{array}$		
Extinction coefficient	0.00434(6)	Not refined		
Residual electron density (min/max), $e/Å^3$	-0.550/0.591	-1.302/2.012		

Table 1. Crystallographic data, experimental details, and refinement parameters for the structures II and III

data for **II** and **III** are summarized in Table 1 and bond lengths and bond angles are in Table 2.

The thermal behavior of **II** and **III** was studied by STA with simultaneous recording of thermogravimetry (TG) and differential scanning calorimetry (DSC) curves. The measurements were performed on an STA 449C Jupiter (NETZSCH) instrument in corundum crucibles with a lid having an opening that ensured a vapor pressure of 1 atm during substance decomposition. The samples were heated to  $1100^{\circ}$ C at a 5°C/min rate in an argon atmosphere. For clearer manifestation of the heat effects, additional measurement in aluminum crucibles were carried out in the initial stage. The sample weight was 3.437 to 4.871 mg. The temperature was measured to an accuracy of  $\pm 0.7^{\circ}$ C and the weight was determined to an accuracy of  $\pm 1 \times 10^{-4}$  mg. In the measurement of TG and DSC curves, a correction file and temperature and sensitivity calibrations for the specified temperature program and heating rate were used. The melting points of the complexes were independently determined on a PTP(M) setup (OSJC Khimlaborpribor).

## **RESULTS AND DISCUSSION**

Table 3 shows the kinetic data on gold(III) binding by chemisorbent I reflecting the variation of the degree of gold sorption on the time of contact of the sorbent with the AuCl<sub>3</sub>-2 M HCl solution in the static mode. A working solution (10 mL) with gold content of 10.84 mg/mL was used. Even in the first minute of the contact, the color of the sorbent precipitates changed from white to yellow-orange and later (by the 10th minute) to light yellow; and the precipitates

# BINDING FORMS OF GOLD(III) FROM SOLUTIONS

Compound II									
Bond	$d, \mathrm{\AA}$	Bond	<i>d</i> , Å						
Au(1)-S(1)Au(1)-S(2)Au(1)Cl(1)S(1)-C(1)S(2)-C(1)N(1)-C(1)	2.3306(2) 2.3310(2) 3.7784(3) 1.7333(10) 1.7242(10) 1.2976(13)	$ \begin{array}{c} N(1)-C(2) \\ N(1)-C(4) \\ Au(2)-Cl(1) \\ Au(2)-Cl(2) \\ Cl(1)\cdots S(1) \end{array} $	1.4776(13) 1.4787(13) 2.2760(3) 2.2714(3) 3.4993(4)						
Angle	ω, deg	Angle	ω, deg						
$\frac{S(1)Au(1)S(2)}{S(1)Au(1)S(2)^{a}}$ Au(1)S(1)C(1) Au(1)S(2)C(1) S(1)C(1)S(2) S(1)C(1)S(2) S(1)C(1)N(1) Angle Au(1)S(1)S(2)C(1)	75.511(8) 104.489(8) 86.41(3) 86.60(3) 111.28(6) 124.34(8) $\phi$ , deg	$ \begin{array}{c} S(2)C(1)N(1) \\ C(1)N(1)C(2) \\ C(1)N(1)C(4) \\ C(2)N(1)C(4) \\ Cl(1)Au(2)Cl(2) \\ Cl(1)Au(2)Cl(2)^{b} \\ \hline \\ Angle \\ S(1)C(1)N(1)C(4) \end{array} $	124.37(8) 120.14(9) 120.84(9) 118.98(8) 90.227(11) 89.773(11) φ, deg						
S(1)Au(1)C(1)S(2)	175.44(5)	S(1)C(1)N(1)C(4) S(2)C(1)N(1)C(2)	-0.11(14)						
S(1)C(1)N(1)C(2)	179.83(8)	S(2)C(1)N(1)C(4)	177.47(8)						
	Compo	ound III							
Molec	cule A	Molec	cule B						
Bond	$d, \mathrm{\AA}$	Bond	<i>d</i> , Å						
Au(1)–S(1) Au(1)–S(2) Au(1) $\cdots$ S(1) <sup>a</sup> Au(1) $\cdots$ S(1) <sup>b</sup> Au(1)–Cl(1) Au(1)–Cl(2) S(1)–C(1) S(2)–C(1) N(1)–C(1) N(1)–C(2) N(1)–C(4) Angle	2.3057(5) $2.2904(5)$ $3.4361(5)$ $3.6329(5)$ $2.3224(5)$ $2.3173(6)$ $1.735(2)$ $1.727(2)$ $1.296(3)$ $1.481(3)$ $1.480(3)$	Au(2)-S(3) Au(2)-S(4) Au(2) $\cdots$ S(4) <sup>c</sup> Au(2) $\cdots$ S(4) <sup>d</sup> Au(2)-Cl(3) Au(2)-Cl(4) S(3)-C(6) S(4)-C(6) N(2)-C(6) N(2)-C(7) N(2)-C(9)	$\begin{array}{c} 2.2919(6) \\ 2.3042(6) \\ 3.4340(7) \\ 3.6398(7) \\ 2.3227(6) \\ 2.3233(6) \\ 1.733(2) \\ 1.729(2) \\ 1.296(3) \\ 1.472(3) \\ 1.485(3) \end{array}$						
	$\omega$ , deg		$\omega, \deg$						
S(1)Au(1)Cl(1) S(1)Au(1)Cl(2) S(2)Au(1)Cl(1) S(2)Au(1)Cl(2)	169.03(2) 172.34(2) 93.30(2)	S(3)Au(2)Cl(4) S(4)Au(2)Cl(3) S(4)Au(2)Cl(3) S(4)Au(2)Cl(4)	93.02(2) 171.93(2) 169.16(2) 96.75(2)						
$\begin{array}{c} Cl(1)Au(1)Cl(2) \\ Au(1)S(1)C(1) \\ Au(1)S(2)C(1) \\ S(1)C(1)S(2) \\ S(1)C(1)S(2) \\ S(1)C(1)N(1) \\ S(2)C(1)N(1) \\ C(1)N(1)C(2) \\ C(1)N(1)C(4) \\ C(2)N(1)C(4) \\ C(2)N(1)C(4) \end{array}$	94.23(2) 87.17(7) 87.85(7) 109.11(11) 125.5(2) 125.4(2) 121.6(2) 120.4(2) 117.7(2)	Cl(3)Au(2)Cl(4)Au(2)S(3)C(6)Au(2)S(4)C(6)S(3)C(6)S(4)S(3)C(6)N(2)S(4)C(6)N(2)C(6)N(2)C(7)C(6)N(2)C(7)C(6)N(2)C(9)C(7)N(2)C(9)	94.09(2) 87.84(7) 87.55(8) 108.87(12) 124.8(2) 126.3(2) 121.4(2) 120.7(2) 117.6(2)						
Angle	φ, deg	Angle 0. deg							
Au(1)S(1)S(2)C(1)           S(1)Au(1)C(1)S(2)           S(1)C(1)N(1)C(2)           S(1)C(1)N(1)C(4)           S(2)C(1)N(1)C(2)           S(2)C(1)N(1)C(4)	$\begin{array}{r} 175.83(12) \\ 176.18(11) \\ -1.5(3) \\ -175.6(2) \\ 176.1(2) \\ 1.9(3) \end{array}$	Au(2)S(3)S(4)C(6) S(3)Au(2)C(6)S(4) S(3)C(6)N(2)C(7) S(3)C(3)N(2)C(9) S(4)C(6)N(2)C(7) S(4)C(6)N(2)C(9)	$\begin{array}{r} -175.45(12) \\ -175.82(11) \\ 2.7(3) \\ 179.5(2) \\ -174.9(2) \\ -1.5(3) \end{array}$						

<b>Table 2.</b> Selected bond lengths ( <i>d</i> ) and bond ( $\omega$ ) and torsion ( $\phi$ ) angles in II* and III**
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\* Symmetry codes: a - x, -y + 1, -z; b - x, -y + 1, -z + 1. \*\* a - x + 3/2, y - 1/2, -z + 1/2; b - x + 3/2, y + 1/2, -z + 1/2; c - x + 1/2, y + 1/2, -z + 1/2; d - x + 1/2, y - 1/2, -z + 1/2.

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Au <sup>3+</sup> concentration, mg/mL (total content, mg)	Sorption degree, $S(\%)$ at contact duration, min					
	1	10	20	30	60	90
10.84 (108.4)	75.65	86.39	87.57	86.42	89.51	90.00

 Table 3. Binding kinetics of gold(III) by sorbent I

became much more bulky. Simultaneously, working solutions were bleached. From the data of sorption experiments, the sorption capacity of I was estimated as 975.6 mg of gold per 1 g of sorbent. When calculated from the formation of complexes II and III, it was somewhat lower, being 963.2 mg. The changes observed during the interaction of sorbent I with a solution of AuCl<sub>3</sub> reflect the successive formation of new compounds. (Earlier, it was found that the initial stage of sorption is accompanied by formation of the ionic complex ([Au{S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}<sub>2</sub>]<sub>2</sub>[Cd<sub>2</sub>Cl<sub>6</sub>])<sub>n</sub> [16].) In order to verify these conclusions, a sample of sorbent I saturated with gold(III) to a limited degree was dissolved in methanol with moderate heating. From the prepared solution, two types of yellow crystals were

obtained simultaneously, namely, thin needles and larger prisms of complexes III and II, respectively.

A <sup>13</sup>C MAS NMR study of selected crystals of different shapes demonstrated that they are spectrally non-identical (Fig. 1). In both cases, the <sup>13</sup>C MAS NMR spectra exhibit resonance signals for the =NC(S)S-,  $-CH_2-$ , and  $-CH_3$  groups (see the Synthesis of II and III). The dithiocarbamate groups, which are most sensitive, to the structural state of the EDtc ligands, are responsible for two (1 : 1) or one <sup>13</sup>C resonance signals (Fig. 1). This implies that III has two groups of non-equivalent EDtc ligands, whereas all ligands of compound II are structurally equivalent. The much lower <sup>13</sup>C chemical shifts of the =NC(S)S– groups in the compounds in question compared with



**Fig. 1.** <sup>13</sup>C CP/MAS NMR spectra of (*a*) needle crystals of **III** and (*b*) prismatic crystals of **II**. The number of acquisitions/sample spinning frequency are 1040/6.7 and 1120/6.1 kHz, respectively.



Fig. 2. Projection of structures (a) II and (b) III on the plane yz. The polymeric chains are arranged along z and y, respectively.

the initial binuclear complex  $[Cd_2\{S_2CN(C_2H_5)_2\}_4]$  are attributable to redistribution of the EDtc ligands into the inner sphere of gold(III). The electron system of gold may be involved more efficiently in the additional shielding of the carbon nuclei of dithiocarbamate groups. Thus, <sup>13</sup>C MAS NMR data attest to the formation in the  $[Cd_2\{S_2CN(C_2H_5)_2\}_4]$ – $[AuCl_4]^-$ –2 M HCl sorption system of two new compounds as individual binding forms of gold from aqueous solutions. This conclusion was verified by solving the structures of **II** and **III** by X-ray diffraction.

The unit cells of II and III comprise 2 and 8 formula units  $[Au{S_2CN(C_2H_5)_2}_2][AuCl_4]$ and  $[Au{S_2CN(C_2H_5)_2}Cl_2]$ , respectively (Fig. 2). In ionic compound II, one gold atom coordinates two structurally equivalent EDtc ligands in the S,S'-bidentate mode, thus forming the centrosymmetric  $[Au{S_2CN(C_2H_5)_2}_2]^+$  cation. The second Au atom in the centrosymmetric [AuCl<sub>4</sub>]<sup>-</sup> anion is surrounded by four. pairwise non-equivalent, chlorine atoms (Au-Cl, 2.2714 and 2.2760 Å). In both coordination spheres, gold forms planar tetragonal chromophores:  $[AuS_4]$  and  $[AuCl_4]$  (low-spin intraorbital  $dsp^2$ -hybrid state of the central gold atom). Complex III has a mixed coordination sphere containing two chlorine atoms along with EDtc. The structure of III comprises two non-equivalent  $[Au{S_2CN(C_2H_5)_2}Cl_2]$  molecules, which are related as conformational isomers in view of the observed differences. In both isomeric molecules, the cis-[AuS<sub>2</sub>Cl<sub>2</sub>] chromophores have a nearly planar structure; all chlorine atoms are structurally non-equivalent (Au–Cl, 2.3173–2.3233 Å).

In both compounds, the coordination of EDtc is close to S,S'-isobidentate (the Au–S bond length is in the narrow range from 2.2904 to 2.3310 Å), the binding strength being somewhat higher in complex **III**. This coordination is accompanied by the formation of

four-membered metal rings [AuS<sub>2</sub>C]. The Au···C distances (2.817, 2.821, and 2.8160 Å) that are much shorter than the sums of the van der Waals radii of these atoms (3.36 Å) [36] point to the existence of *trans*-annular interaction between the gold and carbon atoms. The atoms in the metal rings show a tetrahedral deviation from the planar configuration: the AuSSC and SAuCS torsion angles somewhat (by  $4^\circ$ - $5^\circ$ ) deviate from 180° (Table 2). The diagonal angles SAuCl (169.03°-172.34°) in **III** are also indicative of the distortion of planes of the [AuS<sub>2</sub>Cl<sub>2</sub>] *cis*-chromophores.

Owing to mesomeric effect, the C<sub>2</sub>NC(S)S groups are almost planar: the deviation of the SCNC torsion angles from 180° or 0° does not exceed 5° (Table 2). The N–C(S)S bond length (1.2976 and 1.296 Å), which is intermediate between the typical double C=N (1.27 Å) and single C–N (1.46 Å) bond lengths, reflects a considerable contribution of double bonding and admixing of the  $sp^2$  to  $sp^3$  hybrid state of nitrogen and carbon atoms.

In the structural ordering of complexes II and III at the supramolecular level, the crucial role is played by secondary bonds<sup>3</sup> of three types: Au...S, Au...Cl, and S...Cl. In II, the gold atom of each [Au{S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}]<sup>+</sup> cation forms secondary bonds (Au(1)...Cl(1) 3.7784 Å) with two nearest [AuCl<sub>4</sub>]<sup>-</sup> anions (Fig. 3a). Likewise, each [AuCl<sub>4</sub>]<sup>-</sup> anion interacts with two neighboring cations. This cation—anion binding is additionally enhanced by S(1)...Cl(1) secondary bonds (3.4993 Å) [38]. The described contacts give rise to linear polymeric chains arranged along the z axis (the Au(2)Au(1)Au(2) and Au(1)Au(2)Au(1)

<sup>&</sup>lt;sup>3</sup> The concept of secondary bonds was firstly proposed in [37] to describe interactions between atoms at distances comparable with the sums of their van der Waals radii.



Fig. 3. Pattern of construction of polymeric chains in complexes (a) II and (b) III. The double dashed lines indicate the secondary bonds (a)  $Au \cdots Cl$  and (b)  $Au \cdots S$ ; the dotted line corresponds to (a)  $S \cdots Cl$  secondary bonds.

angles are  $180.00^{\circ}$ ; the Au(1)···Au(2) distance is 5.4832 Å) with the complex cations and anions alternating along the chains (Fig. 2a). The mutual spatial orientation of the neighboring polymeric chains is determined by the secondary bonds, S(1)···Cl(2)<sup>d</sup> and Cl(2)···S(1)<sup>e</sup> of 3.4734 Å (shown by the dotted lines in Fig. 2a), which are even somewhat shorter than the corresponding bonds within the chains (for comparison, the sum of the van der Waals radii of sulfur and chlorine is 3.55 Å [36]).

The supramolecular structure of the mixed-ligand complex **III** is also characterized by 1D polymeric structure (Fig. 2b). However, the polymeric chain is built according to a different principle than that described above for **II**. Since **III** comprises two isomeric [Au{S<sub>2</sub>CN(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>}Cl<sub>2</sub>] molecules, A—Au(1) and B—Au(2), each of them being in contact with two nearest neighbors through pairs of unsymmetrical secondary bonds: Au(1)...S(1)<sup>a/b</sup>, 3.4361/3.6329, and Au(2)...S(4)<sup>c/d</sup>, 3.4340/3.6398 Å (Fig. 3b). (For comparison, the sum of the van der Waals radii of sulfur and gold is 3.46 Å [36].) This gives rise to independent zigzag-like polymeric chains of two types  $(\dots A \dots A \dots A \dots)_n$  and  $(\dots B \dots B \dots B \dots)_n$  with antiparallel isomeric molecules of **III** alternating along the chains. In these chains, the Au(1)–Au(1) and Au(2)–Au(2) distances are 4.27905 and 4.27744 Å, respectively; the Au(1)Au(1)Au(1) and Au(2)Au(2)Au(2) angles are 111.00° and 111.06°, respectively.

To establish the conditions of recovery of the bound gold, thermal behavior of II and III was studied by STA under argon, TG and DSC curves being recorded simultaneously. Generally, the course of TG curves for II and III is roughly the same. We will consider it in more detail in relation to the TG curve for complex III (Fig. 4*a*). The early region of the curve indicates that the compound is thermally stable up to ~170°C. The intensive thermolysis occurs in the narrow range of 170-310°C, which is reflected in the TG curve as a steeply descending part. The next slightly sloping part



Fig. 4. (a) TG and (b, c) DSC curves for complexes (b) II and (a, c) III. (d) Enlarged view of the low-temperature part of DSC curves.

up to  $660^{\circ}$ C is due to desorption of the thermolysis products. For **II**, these parts are somewhat shifted: the major weight loss occurs in the range of  $125-290^{\circ}$ C, indicating simultaneous thermolysis of both the cation and the anion; the subsequent desorption occurs up to ~700^{\circ}C. The weight of the residue at 1100°C was 47.26 or 47.82% of the initial weight for **II** and **III**, respectively, which does not differ significantly from the calculated value (47.33%) for the reduced gold. After opening of the crucible, small pink-orange gold beads 0.005 to 0.05 mm in diameter without visible signs of slag were detected on the bottom.

Despite the similar course of TG curves for II and III, the DSC curves of these complexes are substantially different (Fig. 4b-4d). In the range from 270 to 292°C, the DSC curves (Fig. 4d) show two (II) or three (III) endotherms (with peaks at 277.3, 278.6 and 271.0, 279.0, 291.6°C, respectively), which reflects the complex pattern of the thermal destruction. In the compounds in question, the most probable precursors of the reduced gold are Au<sub>2</sub>S ( $T_{dec} = 240^{\circ}$ C [39]) and AuCl ( $T_{dec} = 289^{\circ}$ C [39]). Therefore, the last (most intense) endotherm noted for complex III should be interpreted as decomposition of AuCl (the extrapolated  $T_{dec}$  of the process is 290.4°C). An independent measurement of the melting point of the complexes (in glass capillaries) showed that at  $\sim 150^{\circ}$ C, the color of sample II changes from light yellow to orange, which is reflected in the DSC curve by a feebly defined effect with a peak at 143.8°C. (This peak is not detected when the curve is recorded repeatedly, which may imply an irreversible phase transition in the sample II.) At ~200°C, the sample of III also changes color from orange to brown. At ~240°C, both samples melt with decomposition (evolution of gas bubbles). In both cases, the high-temperature regions of the DSC

curves show an endotherm reflecting melting of reduced gold: the extrapolated m.p. is 1060.8°C.

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