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Binding of Gold(III) from Solutions with Thallium(I) Dibutyldithiocarbamate: Synthesis, Supramolecular Self-Organization, and Thermal Behavior of the Complex ([Au{S₂CN(C₄H₉)₂}₂][TlCl₄])_n

A. V. Ivanov^a*, O. A. Bredyuk^a, and O. V. Loseva^a

^a Institute of Geology and Nature Management, Far-Eastern Branch, Russian Academy of Sciences, Relochnyi per. 1, Blagoveshchensk, 675000 Russia *e-mail: alexander.v.ivanov@chemist.com

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Abstract—The binding of gold(III) from solution in a 2 M HCl with thallium(I) dibutyl dithiocarbamate leads to the formation of ion-polymeric complex ($[Au\{S_2CN(C_4H_9)_2\}_2][TlCl_4]$)_n, which was studied by (^{13}C , ^{15}N) MAS NMR spectroscopy and X-ray diffraction analysis. In the complex comprising the nonequivalent cations $[Au\{S_2CN(C_4H_9)_2\}_2]^+$ (A and B) and anions $[TlCl_4]^-$, the supramolecular self-assembly is provided by secondary bonds Au···S and S···Cl. The former are involved in the formation of isomeric binuclear cations [A···A] and [B···B] that build the $(···[A···A]···[B···B]···)_n$ polymeric chain; the latter selectively combine the thallium(III) anions and the dimeric cations. Thermolysis of the complex is accompanied by gold recovery and release of TlCl.

Keywords: gold(III) chemisorption, gold(III)-thallium(III) complexes, ion-polymeric compounds, secondary interactions, supramolecular self-organization

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Among thallium dialkyl- and alkylene dithiocarbamates, thallium(I) complexes [1-10] are the most typical, whereas thallium(III) compounds are less common [11–13]. High coordination numbers of thallium(I) predetermine the propensity of its dithiocarbamates to form 1D, 2D, and 3D polymeric structures at the supramolecular level due to nonvalent TI...S and TI...O secondary interactions [1–10, 13–15]. In practical terms, thallium dithiocarbamates are convenient precursors for one-step synthesis of thallium sulfide films and nanothallium sulfides [9, 10, 16-19] and potential candidates for application in microelectronics, nonlinear optics, luminescence, catalysis, ion exchange, etc. [20]. Also, we have recently reported on the use of freshly precipitated thallium(I) dialkyl dithiocarbamates for chemisorption concentration of gold(III) from solutions with preparative isolation of heteropolynuclear complexes [Cl₃Tl(Cl)· $[Au_{2}{S_{2}CN(CH_{3})_{2}}_{4}](CI)TICI_{3}]$ and $([Au_{3}S_{2}CN(C_{2}H_{5})_{2}]_{2}]$. $[TlCl_4]_n$ [21] as individual forms of gold binding.

Here we continued those studies by examining the reactivity of freshly precipitated thallium(I) dibutyl dithiocarbamate (BDtc) having long-chain alkyl substituents towards $[AuCl_4]^-$ anions in solution. Stirring of the polymeric $[Tl_2{S_2CN(C_4H_9)_2}_2]_n$ with a solution of AuCl_3 in 2 M HCl leads to the gradual fixation of gold(III) into the precipitate phase. The chemisorption of gold from the solution and the accompanying redox process caused the formation of gold(III)-thallium(III) ion-polymeric complex $[Au{S_2CN(C_4H_9)_2}_2][TlCl_4])_n$ (1) which was characterized in detail by the methods of (^{13}C , ^{15}N) MAS NMR, X-ray diffraction analysis, and simultaneous thermal analysis. The role of the Au \cdots S and S \cdots Cl secondary bonds and of isomerization of structural units in the supramolecular selforganization of complex 1 was elucidated.

The reaction of freshly precipitated finely-dispersed thallium(I) dibutyl dithiocarbamate $[Tl_2{S_2CN(C_4H_9)_2}_2]_n$ [6], which is characterized by a highly developed surface and a high concentration of coordinatively unsaturated sulfur sites, with a solution of AuCl₃ in 2 M HCl results in the reformation of the precipitate of the original complex with particle coarsening and color change from white to yellow-brown. This was paralleled by discoloration of the working solution, with binding 97.9% of gold from the solution into the solid phase within 1 h. These findings are indi-cative of the formation of new compounds in the system under discussion. We revealed earlier [22] that freshly precipitated thallium(I) dithiocarbamate complexes bind gold(III) from solutions by ion exchange, accompanied by a redox process. Therefore, half of the thallium(I) is oxidized to thallium(III), with the corresponding amount of gold(III) being reduced to the elemental state; the heterogeneous reaction between the initial thallium(I) complex and tetrachloroaurate(III) ions in 2 M HCl can be represented as follows:

$$3[Tl_{2}{S_{2}CN(C_{4}H_{9})_{2}}_{2}] + 5[AuCl_{4}]^{-}$$

= 3[Au{S_{2}CN(C_{4}H_{9})_{2}}_{2}][TlCl_{4}] + 3TlCl + 2Au^{0} + 5Cl^{-}.

The ¹³C MAS NMR spectrum of complex **1** contains resonance signals from =NC(S)S–, =NCH₂–, –CH₂–, and –CH₃ groups of the BDtc ligands. Dithiocarbamate groups that are the most informative for structural studies are represented by two ¹³C resonance signals, whose intensity ratio of 3 : 1 indicates the presence of four nonequivalent BDtc ligands in the structure of **1**. Since the differences in the isotropic chemical shifts $\delta(^{13}C)$ of chemically uniform (though nonequivalent) dithiocarbamate ligands are largely determined by the double bonding contribution to the formally ordinary N–C(S)S bond [23], it may be concluded that the lengths of this bond in the three BDtc ligands are identical (or at least very

Parameter

Fig. 1. Packing of the structural units in a crystal of complex **1** (projection onto the *ab* plane).

close). Nevertheless, the multiplicity of the 13 C resonance signals, observed for other groups, indicates the nonequivalence of these three ligands as well. The 15 N MAS NMR spectrum of the gold(III)-thallium(III) complex includes three resonance signals (1 : 1 : 2), which finding is fully consistent with the existence of four nonequivalent BDtc ligands in the structure of complex **1**. Comparative analysis of the MAS NMR data shows that, for complex **1**, the 13 C and 15 N

Value

Empirical formula *F*(000) C₁₈H₃₆N₂S₄Cl₄AuTl 7200 М 951.86 Crystal size, mm 0.44×0.06×0.06 Crystal system θ range for data collection, deg 2.01-27.10 Monoclinic Space group C2/cRange of reflection indices $-37 \le h \le 37$. $-36 \le k \le 26$, $-19 \le l \le 13$ *a*. Å Measured reflections 29.4240(13) 46232 *b*. Å 28.6084(14) Independent reflections 14016 (*R*_{int} 0.0220) *c*. Å Reflections with $I > 2\sigma(I)$ 11903 15.5746(6) β , deg 103.5380(10) Refinement parameters 513 $V, Å^3$ 12746.0(10) GOF 1.053 Ζ R factors for $F^2 > 2\sigma(F^2)$ 16 R_1 0.0296, wR_2 0.0684 *R* factors for all reflections $d_{\rm calc}, {\rm g/cm}^3$ 1.984 $R_1 0.0395, wR_2 0.0720$ μ . mm⁻¹ Residual electron density (min/max), $e/Å^3$ -2.742/2.40410.257

Parameter

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Table 1. Crystallographic data and experimental and refinement parameters for the structure of complex 1

Value



Bond	d, Å	Bond	d, Å	Bond	d, Å	Bond	<i>d</i> , Å
Cation A							
$Au^1 - S^{11}$	2.3266(13)	$S^{13}-C^{10}$	1.729(5)	$Au^1 \cdots S^{12a}$	3.7838(14)	N^1-C^6	1.478(6)
$Au^1 - S^{12}$	2.3430(13)	$S^{14}-C^{10}$	1.732(5)	$Au^1 \cdots S^{24}$	3.8674(14)	$N^2 - C^{10}$	1.299(6)
$Au^1 - S^{13}$	2.3273(13)	N^1-C^1	1.299(6)	$S^{11}-C^1$	1.725(5)	$N^2 - C^{11}$	1.476(6)
$Au^1 - S^{14}$	2.3345(12)	N^1-C^2	1.481(6)	$S^{12}-C^{1}$	1.731(5)	$N^2 - C^{15}$	1.472(6)
Cation B							
$Au^2 - S^{21}$	2.3356(13)	$S^{23}-C^{28}$	1.726(5)	$Au^2 \cdots S^{11}$	3.3745(13)	$N^{3}-C^{24}$	1.477(7)
$Au^2 - S^{22}$	2.3394(13)	S ²⁴ -C ²⁸	1.722(5)	$Au^2 \cdots S^{22b}$	3.5295(14)	N ⁴ -C ²⁸	1.322(6)
$Au^2 - S^{23}$	2.3518(13)	N ³ -C ¹⁹	1.299(6)	S ²¹ -C ¹⁹	1.728(5)	N ⁴ -C ²⁹	1.464(7)
$Au^2 - S^{24}$	2.3289(13)	$N^3 - C^{20}$	1.489(8)	S ²² -C ¹⁹	1.728(5)	N ⁴ -C ³³	1.464(7)
Anion C				Anion D			
$Tl^{1}-Cl^{11}$	2.3990(16)	$Tl^{1}-Cl^{13}$	2.4120(15)	Tl^2-Cl^{21}	2.4136(14)	$Tl^2 - Cl^{23}$	2.4216(15)
$Tl^{1}-Cl^{12}$	2.4297(13)	Tl ¹ –Cl ¹⁴	2.3816(16)	$Tl^2 - Cl^{22}$	2.3962(17)	Tl ² -Cl ²⁴	2.3960(15)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
Cation A							
$S^{11}Au^1S^{12}$	75.32(4)	$Au^1S^{11}C^1$	86.83(18)	$S^{12}Au^1S^{13}$	178.35(4)	$Au^1S^{14}C^{10}$	86.81(17)
$S^{11}Au^1S^{13}$	103.04(4)	$Au^1S^{12}C^1$	86.17(18)	$S^{12}Au^1S^{14}$	106.32(4)	$S^{11}C^1S^{12}$	111.3(3)
$S^{11}Au^1S^{14}$	177.58(5)	$Au^1S^{13}C^{10}$	87.11(17)	$S^{13}Au^1S^{14}$	75.31(4)	$S^{13}C^{10}S^{14}$	110.7(3)
Cation B							
$S^{21}Au^2S^{22}$	75.28(5)	$Au^2S^{21}C^{19}$	86.70(18)	$S^{22}Au^2S^{23}$	178.10(5)	$Au^2S^{24}C^{28}$	86.42(17)
$S^{21}Au^2S^{23}$	105.81(5)	$Au^2S^{22}C^{19}$	86.58(17)	$S^{22}Au^2S^{24}$	103.38(5)	$S^{21}C^{19}S^{22}$	111.4(3)
$S^{21}Au^2S^{24}$	176.95(5)	$Au^2S^{23}C^{28}$	85.61(18)	$S^{23}Au^2S^{24}$	75.46(5)	$S^{23}C^{28}S^{24}$	112.3(3)
Anion C				Anion D			
$Cl^{11}Tl^1Cl^{12}$	109.44(6)	$Cl^{12}Tl^1Cl^{13}$	109.74(5)	$Cl^{21}Tl^2Cl^{22}$	111.65(6)	$Cl^{22}Tl^2Cl^{23}$	108.17(6)
$Cl^{11}Tl^1Cl^{13}$	105.25(6)	$Cl^{12}Tl^1Cl^{14}$	108.04(5)	$Cl^{21}Tl^2Cl^{23}$	105.11(5)	$Cl^{22}Tl^2Cl^{24}$	110.32(7)
$Cl^{11}Tl^1Cl^{14}$	113.44(7)	$Cl^{13}Tl^1Cl^{14}$	110.89(7)	$Cl^{21}Tl^2Cl^{24}$	113.20(5)	$Cl^{23}Tl^2Cl^{24}$	108.08(6)
Angle	φ, deg	Angle	φ, deg	Angle	φ, deg	Angle	φ, deg
Cation A							
$Au^1S^{11}S^{12}C^1$	173.1(3)	$S^{12}C^1N^1C^2$	169.9(4)	$S^{13}Au^1C^{10}S^{14}$	177.8(3)	$S^{13}C^{10}N^2C^{15}$	178.2(4)
$Au^{1}S^{13}S^{14}C^{10}$	177.6(3)	$S^{12}C^1N^1C^6$	-6.0(7)	$S^{11}C^1N^1C^2$	-10.5(7)	$S^{14}C^{10}N^2C^{11}$	176.0(4)
$S^{11}Au^1C^1S^{12}$	173.8(3)	$S^{13}C^{10}N^2C^{11}$	-2.8(7)	$S^{11}C^1N^1C^6$	173.7(4)	$S^{14}C^{10}N^2C^{15}$	-2.9(7)
Cation B $A_{2}S^{21}S^{22}C^{19} = 177.0(2) = S^{22}C^{19}N^{3}C^{20} = 172.5(5) = S^{23}A_{2}C^{28}S^{24} = 175.0(2) = S^{23}C^{28}N^{4}C^{33} = 179.5(5)$							
Au S S C^{2}	175.4(2)	$5 C^{1}N^{2}C^{2}$	1/3.3(3)	$S AU C^{-}S^{-}$	1/3.9(3)	$5 C IN C^{2}$	-1/8.3(3)
Au $5^{-5}C^{20}$	-1/5.4(3)	$5 C^{1}N^{1}C^{2}$	-5.4(/)	$5 C^{1}N^{2}C^{2}$	-0.1(/)	$5 C N C^{2}$	1/8.4(4)
5-Au ² C ⁻ S ²²	1//.3(3)	5-C-N-C-2	-0./(/)	STUTNUT	1/4.9(4)	5-C-SN-C-55	0.6(7)

Table 2. Selected bond lengths (*d*) and bond (ω) and torsional (φ) angles in complex 1

^a Symmetry transformations: 1/2 - x, 1/2 - y, -z; ^b Symmetry transformations: 1/2 - x, 1/2 - y, 1 - z.



Fig. 2. Structures of (a) isomeric complex cations $[Au\{S_2CN(C_4H_9)_2\}_2]^+$ and (b) complex anions $[TlCl_4]^-$ in complex 1.

isotropic chemical shifts of the =NC(S)S groups change in opposite directions relative to the initial thallium(I) dibutyl dithiocarbamate: $\delta(^{13}C)/\delta(^{15}N)$ are significantly smaller (by 8.1 and 9.0 ppm)/larger (by 13.5, 12.1, and 11.0 ppm). These patterns of the changes and the experimental chemical shifts of ¹³C and ¹⁵N signals from dithiocarbamate groups directly indicate that the formation of complex 1 is accompanied by complete redistribution of the BDtc ligands into the internal coordination sphere of gold(III) [24, 25]. In the latter case the electron density of gold(III) more effectively participates in additional shielding of the carbon nuclei of the =NC(S)S groups belonging to small-sized four-membered cyclic moieties [AuS₂C] (they are involved in trans-annular interaction between the gold and carbon atoms and are characterized by high concentration of delocalized π -electron density). To verify the above conclusions and determine the crystalline and supramolecular structure of complex 1 we applied the direct X-ray diffraction method.

The unit cell of complex **1** includes 16 [Au{S₂CN· (C₄H₉)₂}₂][TlCl₄] formula units (Fig. 1, Table 1). The complex contains two structurally nonequivalent noncentrosymmetric complex cations [Au{S₂CN(C₄H₉)₂}₂]⁺, further referred to as cation A with the Au¹ atom and cation B with the Au² atom (Fig. 2a). As expected from the MAS NMR data, they are formed with the participation of four nonequivalent BDtc ligands, three of which have identical N–C(S)S bond length (1.299 Å, Table 2). Two nonequivalent [TlCl₄]⁻ anions (anion C with Tl¹ and anion D with Tl²) are characterized by distorted tetrahedral geometry: *sp*³-hybrid state of the central thallium atoms (Fig. 2b). The ClTl¹Cl and ClTl²Cl angles for the C and D anions fall within the 105.25°–113.44° and 105.11°–113.20° ranges, respectively (Table 2). Chlorine atoms in these anions are nonequivalent; the length of the Tl–Cl bonds (2.3816–2.4297 Å) agrees with the data from [21, 22, 26]. The character of the structural differences between the nonequivalent complex cations $[Au{S_2CN(C_4H_9)_2}_2]^+$ and anions $[TlCl_4]^-$ allows their classification as conformers.

The BDtc ligands in complex cations A and B have a close to isobidentate coordination (the length of the Au–S bonds lies in the range of 2.3266–2.3518 Å), leading to the formation of two four-membered metal locycles [AuS₂C] with a common gold atom. The interatomic distances Au···C (2.809-2.829 Å) and S···S (2.848–2.864 Å) are much shorter than the sums of the van der Waals radii of the corresponding atomic pairs (3.36 and 3.60 Å) [27], which reflects small sizes of the cyclic moieties. The deviation of the torsion angles AuSSC (173.1°-177.6°) and SAuCS (173.8°-177.8°) from 180° is due to a slight tetrahedral distortion of the planar cycles $[AuS_2C]$. In the $[AuS_4]$ chromophores the central gold atom has a planar tetragonal environment formed by four sulfur atoms (the diagonal angles SAuS lie within 176.95°-178.35°), which corresponds to a low-spin (intraorbital) dsp^2 -hybrid state of gold(III). The atoms in the C₂NCS₂ moieties of the BDtc ligands also slightly deviate from coplanarity, as evidenced by deviation of the SCNC torsional angles from 180° or 0° (Table 2). The N–C(S)S bonds (1.299 and 1.322 Å) are stronger than the N-CH₂ bonds (1.464-1.489 Å) because of admixing of sp^2 - to the sp^3 -hybrid state of the carbon



Fig. 3. A two-membered fragment of the cation-cationic polymeric chain $([Au_2{S_2CN(C_4H_9)_2}_4]^{2+})_n$ oriented along crystallographic axis *c*; dashed lines show the secondary Au…S bonds.

and nitrogen atoms, which determines the contribution of double bonding to the formally ordinary bond due to mesomeric effect of the dithiocarbamate groups.

The structural self-organization of the cationic moiety of the complex at the supramolecular level is achieved via relatively weak nonvalent secondary Au···S interactions. The concept of secondary bonds was proposed in [28] as an attempt to explain the interactions of atoms or groups of atoms at distances comparable with the sums of their van der Waals radii. The uniform isomeric cations $[Au\{S_2CN(C_4H_9)_2\}_2]^+$

are combined by pairs of symmetric secondary bonds Au¹...S^{12a}, Au^{1a}...S¹² 3.7838 Å and Au²...S^{22b}, Au^{2b}...S²² 3.5295 Å, which leads to the formation of two types of binuclear cations $[Au_2{S_2CN(C_4H_9)_2}_4]^{2+}$: $[A \cdots A]$ and $[B \cdots B]$ (Fig. 3). Noncentrosymmetric mononuclear moieties in the cationic dimers are oriented in an antiparallel manner, with displacement of the planes of the [AuS₄] chromophores, thereby minimizing the length of the secondary bonds $Au \cdots S$; the intra-dimer Au–Au distances are 4.831 and 4.318 Å, respectively. Binuclear cations, in turn, form zigzag polymer chains $(\cdots [A \cdots A] \cdots [B \cdots B] \cdots)_n$ due to secondary asymmetric interactions Au¹...S²⁴ 3.8674 Å and $Au^2 \cdots S^{11}$ 3.3745 Å (Fig. 3). In the chain each gold atom achieves a distorted octahedral coordination [AuS₆] (angles $S^{22b}Au^2S^{11}$ 177.26°, $S^{24}Au^1S^{12a}$ 161.50°) via two secondary bonds Au...S; the interdimer Au-Au distance is 4.152 Å, the Au^{2b}Au²Au¹ angle is 133.24°, and Au²Au¹Au^{1a} angles, 123.62°. The binuclear cations $[A \cdots A]$ and $[B \cdots B]$ are mutually oriented in the chain in such a way that the bisecting planes (passing through the both four-membered metallocycles in the adjacent cations A and B) form an angle of ~75°.

Along with the Au···S inter-cation contacts, cationanionic secondary interactions between the isomeric tetrachlorothallate(III) ions $[TlCl_4]^-$ (C and D) and binuclear $[Au_2\{S_2CN(C_4H_9)_2\}_4]^{2+}$ cations ($[A\cdots A]$ and $[B\cdots B]$) are manifested. The selectivity of these interactions consists in the fact that the anion pairs C/D bind binuclear cations $[A\cdots A]/[B\cdots B]$ solely (Fig. 4).



Fig. 4. Mutual binding of isomeric cations $[Au{S_2CN(C_4H_9)_2}_2]^+$ and anions $[TlCl_4]^-$: (a) $C\cdots[A\cdots A]\cdots C$ and (b) $D\cdots[B\cdots B]\cdots D$. The secondary bonds are shown with dashed $(Au\cdots S)$ and dotted $(Cl\cdots S)$ lines.

BINDING OF GOLD(III) FROM SOLUTIONS WITH THALLIUM(I)

Two chlorine atoms in each of the anions C (Tl¹) form secondary bonds S···Cl [29]: S¹²···Cl¹¹ 3.482 Å, S¹⁴···Cl¹¹ 3.297 Å, and S¹³···Cl¹⁴ 3.317 Å with the three sulfur atoms of the binuclear cation [A···A] (Fig. 4a). In a similar way, the anions D (Tl²) and binuclear cations [B···B] form secondary bonds S²¹···Cl²¹ 3.324 Å and S²⁴···Cl²⁴ 3.406 Å (Fig. 4b). The length of the secondary bonds S···Cl is noticeably shorter than the sum of the van der Waals radii of the sulfur and chlorine atoms, 3.55 Å [27]. Thus, pairs of the [TlCl₄]⁻ anions are also involved in the binding of mononuclear moieties in binuclear cations [A···A] and [B···B], additionally stabilizing them.

Thermal behavior of complex 1 was studied by simultaneous thermal analysis involving parallel recording of TG and DSC curves. The compound was thermally stable to ~195°C, above which temperature two steps of mass loss were exhibited by the TG curve. The first stage (~195–285°C) corresponds to the main mass loss, 47.89% of the initial mass, due to active thermolysis of complex 1 at the cation and anion with gold(III) reduction to elemental gold and release of TICI. The expected product of thermolysis of the complex at the anionic moiety is TlCl₃. However, according to the data of [30], at temperatures above 150°C it decomposes into TlCl and chlorine. At ~285°C the TG curve showed the second step of mass loss, primarily associated with evaporation of TlCl ($\Delta m_{calc} =$ 25.20%). The observed mass loss (28.37%) exceeds the calculated value, which indicates the ongoing desorption of thermolysis co-products, proceeding to completion in the subsequent flat part of the TG curve, with the residual mass stabilized at 925°C. The residual mass at 1100°C is 21.54% of the initial value, which slightly exceeds the calculated value (20.69%)for reduced elemental gold. After the thermolysis, small lustrous yellow spheres were found at the bottom of the crucible: based on the energy-dispersion spectral data they were identified as metallic gold.

The low-temperature region of the DSC curve exhibits two endotherms with extrema at 99.9 and 260.8° C, of which the former (extrapolated temperature of 97.3°C) is attributable to the melting of the substance. Independent determination in a glass capillary revealed the corresponding phase transition in the range 96–99°C. The latter extremum is due to thermolysis of complex 1, since it fits exactly onto the first step of the TG curve. The endotherm with extremum at 428.5°C, associated with the second step of the TG curve, is attributable to the melting of the TICl formed (mp 431°C [30]). The high-temperature region exhibits an endothermic peak at 1064.0°, indicative of gold melting.

Thus, binding AuCl₃ from a solution in 2 M HCl by thallium(I) dibutyl dithiocarbamate is accompanied by partial ion exchange, involves a redox process, and leads to the formation of a heteronuclear ion-polymeric gold(III)-thallium(III) complex ($[Au{S_2CN(C_4H_9)_2}_2]$ · [TlCl₄])_n. The supramolecular self-organization of the preparatively isolated complex, as revealed by (¹³C, ¹⁵N) MAS NMR spectroscopy and X-ray diffraction analysis, is based on cation-cationic (Au···S) and cation-anionic (S···Cl) secondary interactions between the isomeric structural units. Examination of the thermal behavior of **1** revealed the quantitative recovery conditions for bound gold(III) and the thermal decomposition pattern.

EXPERIMENTAL

Solid state ¹³C/¹⁵N magic-angle-spinning (MAS) NMR spectra were recorded on a Bruker "Ascend Aeon" NMR spectrometer operating at 100.64/ 40.55 MHz (a superconducting magnet ($B_0 = 9.4$ T) with the closed condensation cycle of helium through an external compressor, and the pulsed Fourier transform mode). Cross-polarization (CP) from the protons was used, and to suppress the ¹³C-¹H and ¹⁵N-¹H interactions, the decoupling effect, with radiofrequency field applied at the resonance frequency of the protons [31]. Polycrystalline sample 1 weighing ~65 mg was placed in a 4.0-mm ZrO₂ ceramic rotor. The ¹³C/¹⁵N MAS NMR measurements were performed using magic angle spinning at 10000(1) Hz; the proton $\pi/2$ pulse durations were 2.7/2.5 µs; ¹H-¹³C/¹H-¹⁵N contact time was 3.0/3.0 ms. For the studied sample, 1024/30458 transients, spaced by relaxation delays of 3.0/3.0 s, were accumulated. The isotropic chemical shifts (ppm) $\delta(^{13}C)/\delta(^{15}N)$ were given relative to one of the components of the external standard, crystalline adamantane (δ 38.48 ppm, relative to tetramethylsilane)/crystalline NH₄Cl (δ 0.0, -341 ppm on an absolute scale [32]), corrected for the magnetic field drift, the frequency equivalent of which was 0.025/0.09 Hz/h.

X-ray diffraction analysis of a needle-shaped single crystal of 1 was performed on a Bruker-Nonius X8 Apex CCD diffractometer (Mo K_{α} radiation, λ 0.71073 Å, graphite monochromator) at 150(2) K. Data were collected using the standard technique: φ and ω scan modes of narrow frames. Absorption correction was applied empirically using the SADABS program [33]. The structure was solved by the direct method and refined by full-matrix least-squares (for F^2) with the anisotropic displacement parameters for nonhydrogen atoms. The hydrogen atoms were located geometrically and refined using the *riding* model. Calculations for structure determination and refinement were performed using SHELXTL program package [33]. The atomic coordinates, bond lengths, and bond angles are deposited with the Cambridge Structural Data Centre (CCDC 1816574) and are freely available at http://www.ccdc.cam.ac.uk. Table 1 lists the main crystallographic data and the structure refinement results for complex 1, and Table 2, the bond lengths, bond angles and torsion angles.

Thermal behavior of complex 1 was studied by simultaneous thermal analysis involving parallel recording of TG and DSC curves. The study was carried out on a STA 449C Jupiter (NETZSCH) instrument in corundum crucibles under a cap with a hole providing a vapor pressure of 1 at for thermal decomposition of the sample. The heating rate was 5°C/min to 1100°C in an argon atmosphere. The sample weight was 1.008-4.882 mg, the temperature was measured accurately to within 0.4°C, and the mass change, to within 1×10^{-4} mg. In recording the TG and DSC curves, a correction file was used, and temperature and sensitivity calibrations for the given temperature program and heating rate were performed. The melting temperature of complex 1 was independently determined on a PTP(M) instrument (OAO "Khimlaborpribor").

The residual substance after thermal analysis was examined on a JSM-35C Jeol analytical scanning electron microscope equipped with a 35-SDS spectrometer with wave dispersion (secondary electron image was used). The elements were qualitatively determined by electron probe X-ray microanalysis using a Rontec energy dispersive spectrometer integrated with a Leo-1420 scanning electron microscope.

Sodium dibutyl dithiocarbamate was prepared by the reaction of carbon disulfide (Merck) with dibutylamine (Aldrich) in an alkaline medium [34], and the initial polymeric thallium(I) dibutyl dithiocarbamate $[Tl_2{S_2CN(C_4H_9)_2}_2]_n$, by quantitative precipitation of TI⁺ ions from the aqueous phase [6]. Individuality of the preparatively isolated salt and of the complex of thallium(I) was proven by ¹³C, ¹⁵N MAS NMR spectrometry (δ , ppm): Na{S₂CN(C₄H₉)₂}·H₂O, 208.3 (-S₂CN=), 55.2 (=NCH₂-), 30.0, 21.0 (-CH₂-), 15.6, 14.9, 14.5 (2 : 1 : 1, -CH₃) [35]; [Tl₂{S₂CN(C₄H₉)₂}₂]_n, 203.4 (-S₂CN=), 54.1, 52.9 (=NCH₂-), 31.0, 30.3, 22.0, 21.6 (-CH₂-), 17.3, 15.9 (-CH₃), 139.1 (=N-) [8].

Ion-polymeric bis(N,N-dibutyldithiocarbamato-S,S')gold(III) tetrachlorothallate(III) ([Au{S₂CN· $(C_4H_9)_2$ [TICl₄])_n (1) was obtained by binding AuCl₃ from a solution in 2 M HCl with freshly precipitated thallium(I) dibutyl dithiocarbamate $[Tl_2{S_2CN(C_4H_9)_2}]$ [8]. The latter was a bulky microcrystalline white precipitate. To 100 mg of polymeric thallium(I) dibutyl dithiocarbamate, 10 mL of the solution of AuCl₃ in 2 M hydrochloric acid containing 40.15 mg of gold was added, and the resulting mixture was stirred for 1 h. The residual gold content in the solutions was determined on a class 1, model 180-50. Hitachi atomic absorption spectrometer. The resulting yellow-brown precipitate was filtered off, rinsed with water, and dried on a filter. The resulting complex was then separated from the precipitate by dissolution in a 1 : 1 acetone-ethanol mixture with moderate heating (30°C), followed by filtration of the solution. For the diffractometric experiment, transparent yellow needleshaped crystals of complex 1 were obtained by evaporating organic solvents at room temperature. ¹³C and ¹⁵N MAS NMR spectra, δ , ppm: 195.3, 194.4 (3 : 1, -S₂CN=); 55.2, 53.7, 53.5, 53.2, 52.6, 52.5 (1 : 1 : 3 : 1 : 1 : 1, =NCH₂-); 31.7, 30.6, 30.1, 29.7, 28.8 (1 : 1 : 3 : 2 : 1, -CH₂-); 21.3, 21.1, 20.9, 20.4, 20.3 (1 : 4 : 1 : 1 : 1, -CH₂-); 14.2, 13.8, 13.4, 13.2, 12.7 (1 : 1 : 2 : 2 : 2, -CH₃); 152.6, 151.2, 150.1 (1 : 1 : 2, =N-).

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CONFLICT OF INTERESTS

No conflict of interest was declared by the authors.

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