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Heterovalent Gold(I,III) Complex ($[Au\{S_2CN(CH_2)_6\}_2]_3[AuCl_2]_2Cl])_n$: Synthesis, Structure, and ^{13}C MAS NMR

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Abstract—The reaction of the freshly precipitated oxovanadium(IV) *cyclo*-hexamethylenedithiocarbamate complex with $[AuCl_4]^-$ anions in a 2 M HCl solution is studied. The water-soluble heterovalent complex $([Au\{S_2CN(CH_2)_6\}_2]_3[AuCl_2]_2Cl])_n$ (**I**) is formed due to the redox reaction. According to the X-ray diffraction data, structure **I** contains two species of complex cations $[Au\{S_2CN(CH_2)_6\}_2]^+$ as conformers performing different structural functions: non-centrosymmetric cations and centrosymmetric cation **B** in a ratio of 2 : 1. Cations **A** form centrosymmetric dimers $[Au_2\{S_2CN(CH_2)_6\}_4]^{2+}$ due to pairs of symmetrical secondary bonds Au···S. The aurophilic Au···Au and secondary Au···S interactions that occur between the complex cations and anions in crystal result in the formation of a polymer network.

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INTRODUCTION

Dialkyldithiocarbamate complexes are widely used in extraction separation and photometric determination and concentration of metals [1, 2]. Another important aspect is the possibility of their use as chemisorbents of metals from solutions, which is due to the stability of dithiocarbamate complexes in acidic media, the developed surface, and a high concentration of dithio groups. The methodical procedures based on chemisorption make it possible to obtain polynuclear and heteropolynuclear compounds variable in composition and structural organization and including gold in different oxidation states (+1 and +3) [3–8]. The gold(I,III) dithiocarbamate complexes form an actively studied group of complex compounds characterized by high cytotoxicity and having potential anticancer activity [9, 10].

The chemisorption systems of the general formula $[M_2\{S_2CN(CH_2)_6\}_4]$ (M = Cd, Zn) have been studied earlier, and the gold complexes of different compositions (homo- and heteropolynuclear) were isolated [11–13].

The interaction of oxovanadium(IV) *cyclo*-hexamethylenedithiocarbamate (Dtc), $[VO\{S_2CN(CH_2)_6\}_2]$ (**Ia**), with a solution of $H[AuCl_4]$ (2 M HCl) was studied in this work. The binding of gold(III) is based on the redox transformations and partial ion exchange. It was experimentally revealed that the heterogeneous reaction resulted in the formation of the water-soluble polynuclear heterovalent complex $[Au\{S_2CN(CH_2)_6\}_2]_3[AuCl_2]_2Cl]_n$ (**I**), whose molecular and supramolecular structures were studied by X-ray diffraction analysis and ^{13}C MAS NMR spectroscopy.

EXPERIMENTAL

Sodium *cyclo*-hexamethylenedithiocarbamate was synthesized by the reaction of carbon bisulfide (Merck) and hexamethyleneimine (Aldrich) in an alkaline medium [14]. The starting compound **Ia** was obtained according to published data [15, 16]. The yield was 72%. According to the data of ^{13}C MAS NMR spectroscopy for $Na\{S_2CN(CH_2)_6\} \cdot 2H_2O$, δ, ppm: 206.3 ($-S_2CN=$); 60.3, 55.5 (1 : 1, $=NCH_2-$); 29.8, 27.0, 26.2, 24.9 (1 : 1 : 1 : 1, $-CH_2-$).

Synthesis of bis(*N*,*N*-*cyclo*-hexamethylenedithiocarbamato-S,S')gold(III) dichloroaurate(I)–chloride (I). A solution (~8 mL) of $AuCl_3$ (in 2 M HCl) containing ~83 mg of gold was poured to freshly precipitated bulky complex **Ia** (100 mg), and the mixture was magnetically stirred for 2 h. The gold content in the solution was determined on an atomic absorption spectrometer (class 1, model 180–50, Hitachi). The formed soluble complex **I** was fractionally extracted with chloroform (an uncolored droplet of $CHCl_3$ indicated the completion of the extraction process). The presence of VO^{3+} in the products was determined by the qualitative reaction with H_2O_2 [17]. To obtain a single crystal, a polycrystalline mixture of compound **I** was recrystallized from acetone.

For $C_{42}H_{72}N_6S_{12}C_{15}Au_5$ (**I**) (M = 2207.86)				
anal. calcd.[#] (%):	C, 22.85;	H, 3.29;	N, 3.81;	S, 17.43.
Found (%):	C, 21.88;	H, 3.37;	N, 3.77;	S, 17.40.

[#] Elemental analysis was carried out on a Carlo Erba EA 1108 automated analyzer.

According to the data of ^{13}C MAS NMR spectroscopy for **I**, δ, ppm: 194.6, 193.3 (2 : 1, $-S_2CN=$); 55.7, 54.2, 53.7, 52.4 ($=NCH_2-$); 28.6, 27.4, 26.2, 25.2 ($-CH_2-$). Crystalline adamantane was used as an external standard: a reference signal with $\delta =$ 38.48 ppm [18] relative to tetramethylsilane.

The ^{13}C MAS NMR spectrum of I was recorded on a CMX-360 spectrometer (Agilent/Varian/Chemagnetics InfinityPlus) with a working frequency of 90.52 MHz, a superconducting magnet with $B_0 =$ 8.46 T, and Fourier transform. Proton cross polarization was used. The decoupling effect using a radiofrequency field at the resonance frequency of protons [19] was applied for $^{13}C-^{1}H$ interaction decoupling. A sample (~100 mg) was placed in a 4.0-mm ceramic ZrO_2 rotor. When measuring ^{13}C MAS NMR spectra, rotation at a magic angle, a scan number of 20 000, a duration of proton $\pi/2$ pulses of 5.0 μs, a $^{1}H-^{13}C$ contact time of 2.5 ms, and an interval between pulses of 3.0 s were used. Isotropic chemical shifts of ^{13}C (δ, ppm) are given relative to one of the components of the external standard (crystalline adamantane, $\delta =$ 38.48 ppm relative to tetramethylsilane).

The X-ray diffraction analysis was carried out from a single crystal of **I** on a BRUKER SMART APEX II CCD diffractometer (MoK_α-radiation, $\lambda = 0.71073$ Å, graphite monochromator) at 150(2) K [20]. A semiempirical absorption correction was applied to the data obtained [21]. The structure was solved by a direct method, and all non-hydrogen atoms were localized in electron density difference syntheses and refined for F^2_{hkl} in the anisotropic approximation. Hydrogen atoms were localized in electron density difference syntheses, and other hydrogen atoms were placed in geometrically calculated positions. The calculations were performed using the SHELX-97 program package [22]. The crystallographic parameters and structure refinement details are the following: needle-like yellow crystals, 0.60 × 0.05 × 0.03 mm, monoclinic crystal system, space group $C2/c$, $a =$ 34.21032, $b = 6.6280(3)$, $c = 15.27(3)$ Å, $\beta =$ 119.1080(10)°, $V = 6115.6(5)$ Å^3, $Z = 4$, $\rho_{calcd} =$ 2.398 g/cm^3, $\mu = 12.618$ mm^{-1}, $\theta = 1.51°-25.25°$, ranges of reflection indices: $-44 \leqslant h \leqslant 43$, $-8 \leqslant k \leqslant 7$, $-38 \leqslant l \leqslant 40$, number of measured reflections 14692, number of independent reflections 6772, $R_{int} = 0.022$, GOOF = 1.033, R_1 ($I > 2\sigma(I)$) = 0.0245, wR_2 ($I > 2\sigma(I)$) = 0.0517, $T_{min}/T_{max} = 0.0492/0.7033$, and residual electron density (min/max) $-1.251/1.613$ e Å^{-3}. The atomic coordinates, temperature factors, and full data on the geometric parameters were deposited with the Cambridge Crystallographic Data Centre (CIF file CCDC 1420448; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Upon the interaction of the starting compound **Ia** with a solution of $AuCl_3$ (in 2 M HCl), bleaching of the reaction solution was observed within the first minutes of contact, and the gray color of the initial complex gradually changed by the yellow color: in 30–35 min from the onset of experiment, the bulky precipitate changed with a decrease in the particle size (a flaky precipitate became finely dispersed) and the solution gained an emerald tint. Thus, the character of the mentioned changes indicates the formation of new compounds (in both the precipitate and solution).

The observed redox reaction presumably is the following[1]:

$$\begin{gathered}4[VO\{S_2CN(CH_2)_6\}_2] + 7H[AuCl_4] \\ = [Au\{S_2CN(CH_2)_6\}_2]_3[AuCl_2]_2Cl \\ 2[Au\{S_2CN(CH_2)_6\}Cl_2] + 4VOCl_3 + 7HCl.\end{gathered}$$

The possibility of the simultaneous formation of several products from different phases was observed earlier [8]. The degree of binding of gold from solution was ~99%.

The unit cell of complex **I** contains four formula units $[Au\{S_2CN(CH_2)_6\}_2]_3[AuCl_2]_2Cl$ (Fig. 1). The cationic part of compound **I** is presented by two types of complex ions $[Au\{S_2CN(CH_2)_6\}_2]^+$: hereinafter, cation **A** with the Au(1) atom and cation **B** with the Au(2) atom in a ratio of 2 : 1 (table). In each cation, each gold atom coordinates two dithiocarbamate ligands through the S,S'-bidentate mode to form the square chromophore $[AuS_4]$ (low-spin intraorbital dsp^2-hybrid state). Cations **A** are non-centrosymmetric, unlike cetrosymmetric cations **B**. It follows from this that structure **I** contains three nonequivalent Dtc groups, which is consistent with the ^{13}C MAS NMR data (see further). Cations **A** and **B** are is characterized by the anisobidentate coordination mode (the Au–S bond lengths range from 2.3260 to 2.3417 Å).

The discussed structural differences make it possible to consider cations **A** and **B** as conformers. The

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[1] Heteroleptic complex $[Au\{S_2CN(CH_2)_6\}Cl_2]$ that was isolated from a solid phase is a structural analog of compounds $[Au(S_2CNR_2)Cl_2]$ ($R = C_2H_5$; $R_2 = (CH_2)_5$), which were prepared and described previously [4, 23].

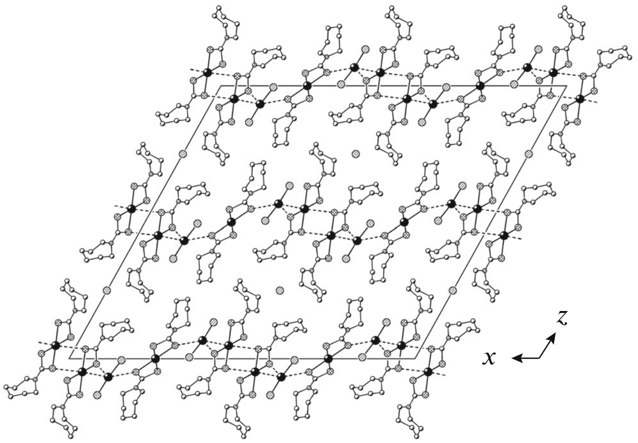

Fig. 1. Projection of structure **I** onto the plane *xz* (secondary interactions are shown by dashed lines).

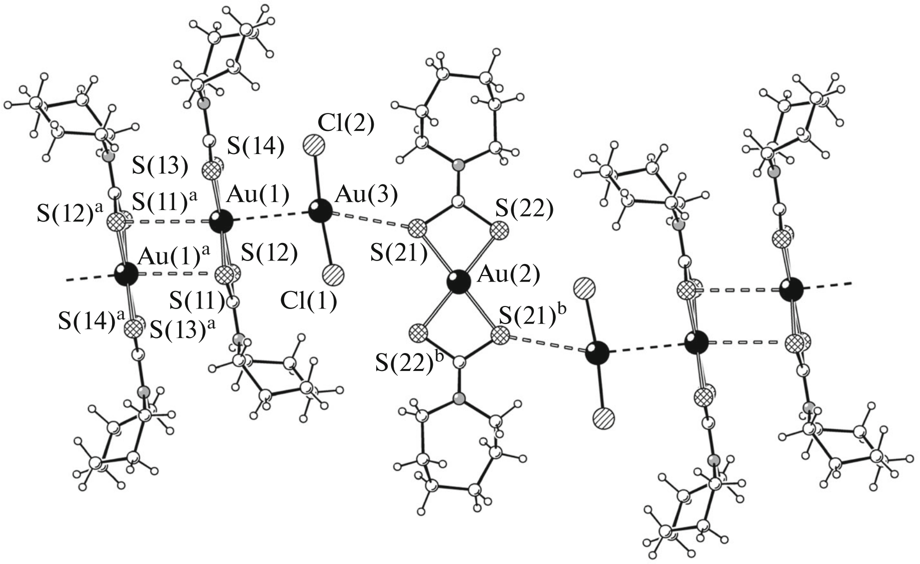

Fig. 2. Fragment of the polymer chain including the binuclear $[Au_2\{S_2CN(CH_2)_6\}_4]^{2+}$ (with the Au(1) atom) and mononuclear $[Au\{S_2CN(CH_2)_6\}_2]^+$ (with the Au(2) atom) cations (secondary bonds are shown by dashed lines).

dithiocarbamate complex rather frequently exhibits conformational isomerism [23–25].

The gold atom forms a four-membered metallocycle $[AuS_2C]$ with each Dtc ligand in $[Au\{S_2CN(CH_2)_6\}_2]^+$. The interatomic distances Au···C (2.813–2.842 Å)/S···S (2.858–2.866 Å) are significantly less than the sum of the van der Waals radii (3.36/3.60 Å), respectively [26–28]. The substantial bringing together of the gold and carbon atoms is due to the manifestation of the *trans*-annular interaction and a high concentration of the π-electron density inside the cycles.

The $[AuS_2C]$ groups in cation **B** are nearly planar, unlike cation **A** in which the AuSSC and AuSCS torsion angles in these cycles deviate from 180°. In the $[AuS_4]$ chromophores of both cations **A** and **B**, the diagonal SAuS angles deviate from 180°, indicating their orthorhombic distortion (table).

The gold atoms in cation **A** form centrosymmetrical binuclear structures[2] $[Au_2\{S_2CN(CH_2)_6\}_4]^{2+}$ due to pairs of symmetrical secondary bonds[2] Au(1)···S(12*A*) and Au(1*A*)···S(12) (3.6137 Å). In the dimeric cations, the cyclic groups of pairs of ligands Dtc are in the *cis* position relative to the plane of the chromophore $[AuS_4]$, whereas they occupy the *trans* position in the mononuclear cation **B** (Fig. 2).

The analysis of the crystal packing shows that the dimeric and monomeric cations (between which the

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[2] The concept of secondary bonds was first proposed [29] for the description of interactions between the atoms at distances comparable with the sum of their van der Waals radii.

Selected bond lengths and bond (ω) and torsion (φ) angles in structure **I***

Bond	*d*, Å	Bond	*d*, Å
	Cation **A**		
Au(1)–S(11)	2.3260(11)	S(14)–C(8)	1.723(5)
Au(1)–S(12)	2.3408(11)	N(1)–C(1)	1.309(6)
Au(1)–S(13)	2.3344(11)	N(1)–C(2)	1.475(6)
Au(1)–S(14)	2.3415(12)	N(1)–C(7)	1.483(5)
S(11)–C(1)	1.725(5)	N(2)–C(8)	1.313(6)
S(12)–C(1)	1.733(5)	N(2)–C(9)	1.473(6)
S(13)–C(8)	1.733(5)	N(2)–C(14)	1.485(6)
	Cation **B**		
Au(2)–S(21)	2.3382(10)	N(3)–C(15)	1.291(5)
Au(2)–S(22)	2.3417(11)	N(3)–C(16)	1.488(5)
S(21)–C(15)	1.742(5)	N(3)–C(21)	1.488(5)
S(22)–C(15)	1.738(4)		
	Anion		
Au(3)–Cl(1)	2.2829(12)	Au(3)–Cl(2)	2.2811(13)
Angle	ω, deg	Angle	ω, deg
	Cation **A**		
S(11)Au(1)S(12)	75.55(4)	Au(1)S(11)C(1)	86.77(16)
S(11)Au(1)S(13)	102.70(4)	Au(1)S(12)C(1)	86.11(15)
S(11)Au(1)S(14)	176.54(4)	Au(1)S(13)C(8)	86.17(16)
S(12)Au(1)S(13)	178.22(4)	Au(1)S(14)C(8)	86.16(16)
S(12)Au(1)S(14)	106.17(4)	S(11)C(1)S(12)	111.5(2)
S(13)Au(1)S(4)	75.60(4)	S(13)C(8)S(14)	112.0(3)
	Cation **B**		
S(21)Au(2)S(22)	75.41(4)	Au(2)S(22)C(15)	86.96(16)
S(21)Au(2)S(22)[c]	104.59(4)	S(21)C(15)S(22)	140.6(2)
Au(2)S(21)C(15)	86.98(13)		
	Anion		
Cl(1)Au(3)Cl(2)	173.43(4)	Cl(2)Au(3)S(11)[b]	79.12(4)
Cl(1)Au(3)S(11)[b]	103.09(4)		
Angle	φ, deg	Angle	φ, deg
	Cation **A**		
Au(1)S(11)S(12)C(1)	176.6(3)	S(11)C(1)N(1)C(7)	180.0(3)
Au(1)S(13)S(14)C(8)	−178.2(3)	S(13)C(8)N(2)C(9)	−2.6(7)
S(11)Au(1)C(1)S(12)	177.0(3)	S(13)C(8)N(2)C(14)	179.7(4)
S(13)Au(1)C(8)S(14)	−178.4(3)	S(14)C(8)N(2)C(9)	175.8(4)
S(11)C(1)N(1)C(2)	−0.4(6)	S(14)C(8)N(2)C(14)	−1.9(7)
	Cation **B**		
Au(2)S(21)S(22)C(15)	180.0(3)	Short contacts	
S(21)Au(2)C(15)S(22)	180.0(2)	Au(1)···Au(3)	3.4409(3)
S(21)C(15)N(3)C(16)	−0.2(6)	Au(1)···S(12)[a]	3.6137(12)
S(21)C(15)N(3)C(21)	−175.8(3)	Au(3)···S(21)[a]	3.4388(11)
S(21)C(15)N(3)C(16)	−179.6(3)	Au(3)···S(11)[b]	3.2320(12)
S(22)C(15)N(3)C(21)	4.8(6)		

* Symmetry transforms: [a] −*x*, 1 − *y*, −*z*; [b] *x*, 1 + *y*, *z*; [c] 1/2 − *x*, 5/2 − *y*, −*z*.

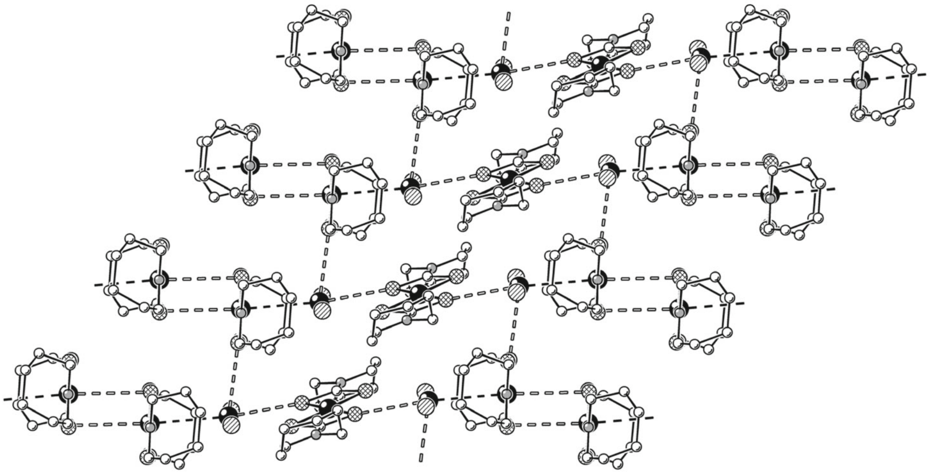

Fig. 3. Formation of 2D polymer structure **I**.

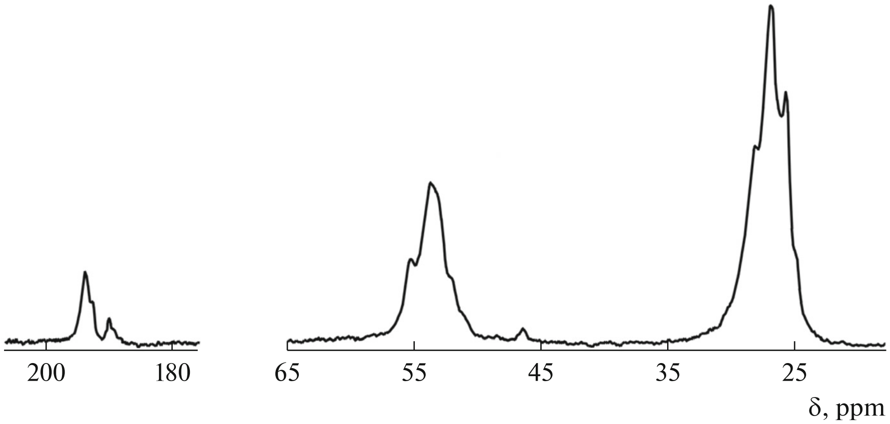

Fig. 4. MAS ^{13}C NMR spectrum of complex **I** (scan number, duration of proton π/2 pulses, and contact time ^{1}H–^{13}C are 20000, 5.0 μs, and 2.5 ms, respectively).

linear anions $[AuCl_2]^-$ are arranged (Cl(1)Au(3)Cl(2) 173.43(4)°) form a supramolecular chain due to the aurophilic (Au(1)···Au(3) 3.441 Å) and secondary Au···S and S···Cl (Au(3)···S(21) 3.439, S(12)···Cl(1) 3.834, S(13)···Cl(2) 3.426, S(14)···Cl(2) 3.657, S(21)···Cl(1) 3.411 and S(22)···Cl(1) 3.548 Å) interactions (Figs. 2, 3). The adjacent chains are joined into a polymer layer by the strongest secondary bonds Au(3)···S(11*B*) 3.232 Å (Fig. 3).

The ^{13}C MAS NMR spectrum of polycrystals **I** exhibits resonance signals of the =NC(S)S–, =NCH2–, and –CH2– groups (Fig. 4). The chemical shifts ^{13}C of the =NC(S)S– groups are characterized by somewhat lower values than those in similar systems studied earlier [12, 13]. This can be explained by a more efficient participation of the electronic system of the central gold atom in the additional shielding of the carbon nuclei of the =NC(S)S– groups. In a range of =NC(S)S– groups, two resonance signals ^{13}C with relative intensities of 2 : 1 reflect correctly three nonequivalent dithiocarbamate groups in structure **I**. Beside that, experimental 13C MAS NMR spectrum discover some amount of unidentified admixture in polycrystalline sample of **I**.

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