

CRYSTAL STRUCTURE OF NITRATE

tris(4-ALLYLTHIOSEMICARBAZIDE)-

CHROMIUM(III) HYDRATE

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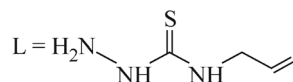
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The crystal structure of nitrate tris(4-allylthiosemicarbazide)chromium(III) hydrate $[\text{CrL}_3](\text{NO}_3)_3(\text{H}_2\text{O})_{1.05}$ (**I**), where L is 4-allylthiosemicarbazide, is determined. The asymmetric unit of the cell of the crystal structure of **I** contains a complex of a chromium ion with three bidentate coordinated molecules L. The outer coordination sphere of the central atom contains a disordered water molecule and three nitrate ions. The coordination polyhedron of the chromium atom in complex **I** is an octahedron. In the crystal, the complexes of the compound under study are joined with each other by the outer-sphere nitrate groups into a three-dimensional branched net of hydrogen bonds.

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Thiosemicarbazide and its derivatives form stable coordination compounds with nearly all transition metals. Many of such substances exhibit biological activity. It is determined [1-4] that these properties of the complexes are in good agreement with their structure. Due to this fact, the synthesis and study of the structural features of new coordination compounds of metals with thiosemicarbazide derivatives are of both scientific and practical interest.



The objective of this work is to synthesize and determine the structural features of hydrate of tris(4-allylthiosemicarbazide)chromium(III) nitrate $[\text{CrL}_3](\text{NO}_3)_3(\text{H}_2\text{O})_{1.05}$ (**I**), where L is 4-allylthiosemicarbazide.

Experimental. Compound **I** was synthesized according to the following procedures: a solution containing 30 mmol of 4-allylthiosemicarbazide in 30 ml of ethanol was added to a solution containing 10 mmol of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in 20 ml of ethanol while stirring and heating on a water bath (50-55°C). As a result, a violet solution is formed, from which the fine crystalline precipitate slowly formed in a day (the yield was 65%). It was filtered off on a glass filter, washed with a small amount of ethanol, ether and dried in the air. Its composition was determined using the elemental analysis data.

Found, %: C 23.70, H 4.48, N 25.47, S 14.57, Cr 7.78. For $\text{C}_{12}\text{H}_{29.1}\text{N}_{12}\text{O}_{10.05}\text{S}_3\text{Cr}$, calculated, %: C 22.16, H 4.51, N 25.84, S 14.79, Cr 7.99.

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Compound **I** is well soluble in dimethylformamide, dimethylsulfoxide, water, and alcohols. Its single crystals suitable for the X-ray crystallographic analysis were obtained by recrystallization of the compound under study from ethanol.

The single crystal X-ray diffraction analysis of complex **I** was carried out on an Xcalibur diffractometer (Oxford Diffraction) [5]. The structure was solved by the direct method and refined anisotropically by the full-matrix least-squares techniques for non-hydrogen atoms using the SHELX-97 program [6]. The hydrogen atoms were placed in geometrically idealized positions, and their thermal parameters U_H were considered to be 1.2 times as much as those of the carbon and oxygen atoms bonded to them. The coordinates of the basic atoms of the structures under study have been deposited with the Cambridge Crystallographic Data Centre (CCDC 1004563). The geometric calculations and figures were carried out using the PLATON program [7]; the structure packings are shown only with those hydrogen atoms that participate in hydrogen bonds. The Cambridge Structural Database (version 5.30) [8, 9] was used to analyze the obtained structures. The main parameters of the experiment, solutions and refinements of the structures are as follows: $C_{12}H_{29.1}N_{12}O_{10.05}S_3Cr$, sample dimensions $0.23 \times 0.16 \times 0.04$ mm, MoK_{α} radiation $\lambda = 0.71073$ Å, $M = 1297.08$, monoclinic crystals, space group $P2_1/c$, $a = 11.4367(6)$ Å, $b = 12.9097(6)$ Å, $c = 19.5571(7)$ Å, $\beta = 92.430(4)^\circ$, $V = 2884.9(2)$ Å³; $Z = 2$, $\rho_{calc} = 1.493$ g/cm³, $\mu = 0.678$ mm⁻¹, 9396 reflections measured ($\theta_{max} = 25.05^\circ$), 5096 independent, 1571 with $I > 2\sigma(I)$, 349 parameters refined, for $I > 2\sigma(I)$ $R_1 = 0.0537$ and $wR_2 = 0.1019$, $\Delta\rho$ (max / min) = $0.426 / -0.284$ e/Å³.

Results and discussion. The asymmetric unit of the cell of the crystal structure of **I** contains a complex of a chromium ion with three bidentate coordinated molecules L (Table 1.). The outer coordination sphere of the central atom contains a disordered water molecule and three nitrate ions (Fig. 1). The coordination polyhedron of the chromium atom in complex **I** is an octahedron; the Cr–S and Cr–N bond lengths of the central atom with the donor atoms of the bidentate ligands are pairwise 2.336(2) Å and 2.342(2) Å, 2.340(2) Å and 2.087(5) Å, and 2.091(5) Å and 2.103(5) Å respectively. The angles at the chromium atom formed by these bonds are in the range of $171.5(1) \div 173.6(2)^\circ$ and $83.1(2) \div 93.7(2)^\circ$. The volume of the coordination polyhedron of the chromium atom in the complex is 14.411 Å³. The metal rings of compound **I** are bent along the S...N line; the angles between the (Cr(1)S(1)N(1)) and (S(1)N(1)N(2)C(1)) planes are 8.7° , 10.2° , and 9.4° respectively for ligands A, B, C. At the same time, ligands A, B, C are not planar, the angle between the planes of the (S(1)N(1)N(2)C(1)) and (N(3)C(2) C(3) C(4)) moieties are 76.1° , 75.3° , and 83.5° . In the crystal, the complexes of the compound under study are joined with each other by outer-sphere nitrate groups into a three-dimensional branched net of hydrogen bonds (Fig. 2). Wherein, according to the criterion proposed in [7] ($H \cdots Cg < 3.0$ Å, $\gamma < 30.0^\circ$, where γ is the angle between the HCg vector and the normal to the aromatic ring), the X–H...Cg (Cr(1)S(1)N(1)N(2)C(1)) (x, y, z) (π ring) interaction takes place in the crystal packing of the compound under study. Thus, for the N(1B)–H1BA...Cg interaction, the distance between the hydrogen atoms and the centroids of the metal rings is 2.79 Å, and the value of γ is 29.7° .

TABLE 1. Some Interatomic Distances and Bond Angles for Compound **I**.

Bond	A (d, Å)	B (d, Å)	C (d, Å)	Bond	A (d, Å)	B (d, Å)	C (d, Å)
Cr(1)–S(1)	2.336(2)	2.342(2)	2.340(2)	N(1)–N(2)	1.398(7)	1.420(6)	1.412(6)
Cr(1)–N(1)	2.087(5)	2.091(5)	2.103(5)	N(2)–C(1)	1.320(8)	1.343(8)	1.333(8)
S(1)–C(1)	1.716(7)	1.710(7)	1.700(6)	N(3)–C(1)	1.318(8)	1.303(8)	1.317(7)
Angle	ω , deg	Angle	ω , deg	Angle	ω , deg	Angle	ω , deg
N(1A)–Cr(1)–N(1B)	91.3(2)	N(1C)–Cr(1)–S(1C)	83.12(15)	N(1A)–Cr(1)–S(1B)	93.74(15)		
N(1A)–Cr(1)–N(1C)	91.6(2)	N(1A)–Cr(1)–S(1A)	83.17(16)	N(1B)–Cr(1)–S(1B)	83.24(15)		
N(1B)–Cr(1)–N(1C)	93.1(2)	N(1B)–Cr(1)–S(1A)	171.53(16)	N(1C)–Cr(1)–S(1B)	173.59(16)		
N(1A)–Cr(1)–S(1C)	172.87(16)	N(1C)–Cr(1)–S(1A)	93.50(16)	S(1C)–Cr(1)–S(1B)	91.86(8)		
N(1B)–Cr(1)–S(1C)	93.73(16)	S(1C)–Cr(1)–S(1A)	92.36(9)	S(1A)–Cr(1)–S(1B)	90.68(8)		

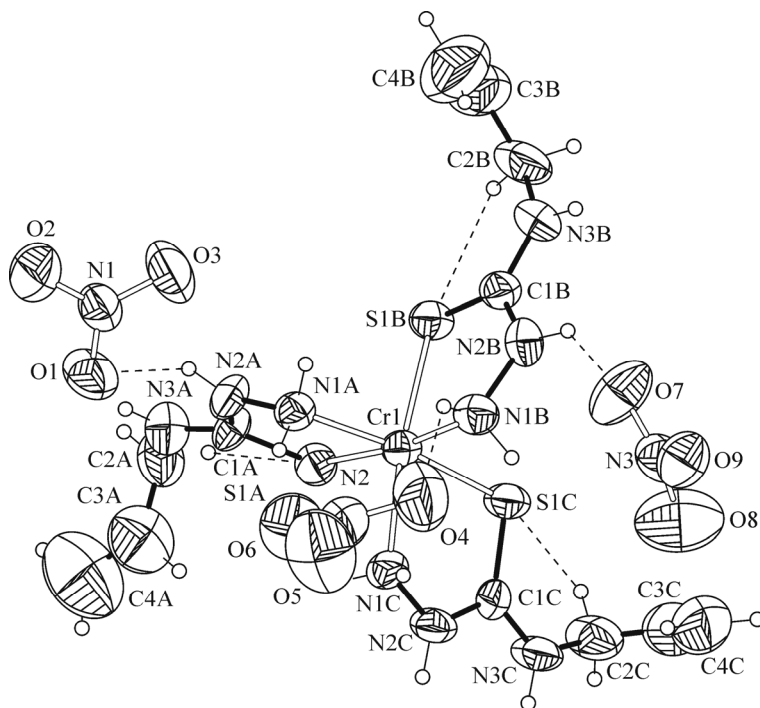


Fig. 1. Atomic numbering in the complex of compound **I**.

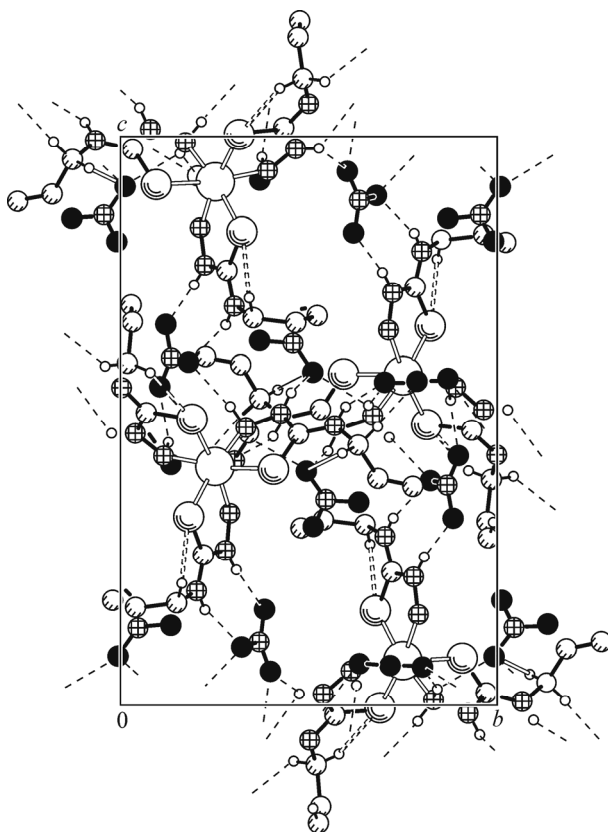


Fig. 2. Fragment of the packing of compound **I** in the crystal.

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