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Original Scientific Article

The Rare Examples of Thiosemicarbazonato Chromium(III) Complexes: Crystal Structures of $[Cr(Hsal\ 4\text{-}Metsc)_2]Cl{\cdot}CH_3OH$ and $[Cr(Hsal\ 4\text{-}Phtsc)_2]Cl$†

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Abstract. Reactions of salicylaldehyde 4-methylthiosemicarbazone (H_2L^1) and salicylaldehyde 4-phenylthiosemicarbazone (H_2L^2) with assorted chromium(III) precusors, $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_6](NO_3)_3{\cdot}3H_2O$ and $[Cr(H_2O)_6](CH_3COO)_3$, afforded new mononuclear chromium(III) complexes of the general formula $[Cr(HL)_2]X$ ($X = Cl^-$, NO_3^- and CH_3COO^-). In all isolated compounds, Cr(III) ion is coordinated by the *O,N,S* atoms of the two singly deprotonated thiosemicarbazonato ligands, which are present in the thione form. All complexes have been characterized in the solid-state by means of chemical analyses, TG analysis and IR spectroscopy. The crystal and molecular structures of $[Cr(Hsal\ 4\text{-}Metsc)_2]Cl{\cdot}CH_3OH$ and $[Cr(Hsal\ 4\text{-}Phtsc)_2]Cl$ have been determined on the basis of single-crystal X-ray diffraction data. In accordance with kinetic inertness of neutral chromium(III) complexes all our attempts to prepare thiosemicarbazonato complexes *via* ligand-exchange reaction with $[Cr(acac)_3]$ have been unsuccessful.(doi: 10.5562/cca2153)

Keywords: Chromium(III) complexes of thiosemicarbazones

INTRODUCTION

Investigation of transition metal complexes and understanding their function in biological systems is a challenging research area. One of the most controversial transition metal in term of biological activities is chromium. The first data about one chromium(III) complex as a biological molecule was published in 1950. by K. Schwarz and W. Mertz.[1] The results of their experiments on nutrient-deficient rats suggested that $[Cr(pic)_3]$ (pic = 2-pyridinecarboxylate) could act as „glucose tolerance factor".[2] Since then a lot of studies on isolation and characterization of Cr(III) compounds containing biological active substance were made.[3] For example, numerous Cr(III)-binding proteins were identified in yeast extracts.[4] Nowadays, toxicological studies showed that the nature of the ligand is one of the crucial factors that determine the toxicity of Cr(III) biological molecules, and these effects were studied in relation to ligand-exchange and redox reactions. Cr(III) complexes are kinetically inert[5] and this is one of their main chemical properties that could be responsible for toxicity through altering structures and functions of membranes, proteins and nucleic acids.[6]

Thiosemicarbazones, an important class of sulphur-donor Schiff bases, continue to draw considerable attention, mostly because of their intriguing coordinating abilities and biochemical properties.[7,8] Our group has contributed to the field with a number of studies, among which the most numerous are those dedicated to the chemistry of thiosemicarbazonato molybdenum(VI) and molybdenum(V) complexes.[9] The propensity of thiosemicarbazones to exist as thione-thiole tautomers defines their behavior in many ways and allows them to bind to metal cations in a variety of coordination modes.[10] This can be well illustrated with a group of *ONS*-thiosemicarbazonato chromium(III) complexes: $Ba[Cr(C_4H_5N_3O_2S)_2]{\cdot}5H_2O$,[11] in which the ligands are coordinated in the thiole form; $[Cr(Hsaltsc)_2]ClO_4{\cdot}3H_2O$[12] ($H_2$saltsc = salicylaldehyde thiosemicarbazone) in which the two ligands are coordinated in the thione form; $[Cr(HKbtsc)(Kbtsc)]$[13] (H_2Kbtsc = 2-ketobutyric acid thiosemicarbazone) and $[Cr(Hthpu)(thpu)]{\cdot}H_2O$[14] ($H_2$thpu = pyruvic acid thiosemicarbazone) in which ligands are bound in different tautomeric forms. Although these examples clearly demonstrate the tautomeric flexibility of thiosemicarbazones as ligands, with only few thus far reported complexes it is not feasible to derive some general conclusions on the causes

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Table 1. Crystallographic data for **1** and **4**

	1	**4**
Chemical formula	$C_{19}H_{24}N_6O_3S_2ClCr$	$C_{28}H_{24}N_6O_2S_2ClCr$
M_r	536.01	628.10
Crystal system, color and habit	Triclinic, dark red-brown, prism	Monoclinic, dark red-brown, prism
Crystal dimensions (mm^3)	0.14×0.38×0.75	0.05×0.14×0.19
Space group	$P\bar{1}$	Cc
Z	2	4
Unit cell parameters:		
a (Å)	8.5698(3)	19.877(2)
b (Å)	11.4511(4)	11.7010(9)
c (Å)	11.7279(4)	12.6736(12)
α (°)	95.246(3)	90
β (°)	93.442(3)	106.398(11)
γ (°)	97.042(3)	90
V ($Å^3$)	1134.48(7)	2827.7(5)
T (K)	103(2)	295(2)
μ (mm^{-1})	0.841	0.685
F(000)	554	1292
D_{calc} (g cm^{-3})	1.569	1.475
No. refined parameters, N_p /restraints	307/5	373/6
Reflections collected, unique,	13629, 4677, 0.024, 4092	9012, 4856, 0.040, 3626
R_1[a][$I \geq 2\sigma(I)$]/wR_2[b] (all data)	0.0391/0.1019	0.0532/0.1211
Goodness of fit on F^2, S[c]	1.077	1.034
Max., min. electron density (e $Å^{-3}$)	0.54, –0.46	0.37, –0.27

[a] $R = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$; $w = 1/[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]$ where $P = (F_o^2 + 2F_c^2)/3$.
[b] $wR = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.
[c] $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(N_r - N_p)\}^{1/2}$ where N_r = number of independent reflections, N_p = number of refined parameters.

of such structural differences. However, it motivated us to inspect more closely the chemistry of chromium(III) with thiosemicarbazone ligands. For that we have chosen to investigate the reactions of salicylaldehyde 4-methylthiosemicarbazone (H_2L^1) and salicylaldehyde 4-phenylthiosemicarbazone (H_2L^2), and assorted chromium(III) precursors (nitrato, acetato and chlorido chromium(III) salts as well as tris(acetylacetonato)chromium(III) complex). As a result, we herein report series of novel chromium(III) complexes of the general formula $[Cr(HL)_2]X$ (X = Cl^-, NO_3^- and CH_3COO^-), all of which have been characterized in the solid state by means of chemical analyses, TG analysis and IR spectroscopy. In the case of chloride complexes, single-crystal X-ray diffraction has been additionally employed and has revealed interesting hydrogen bonding patterns within their crystal structures.

EXPERIMENTAL

Materials and Methods

Salicylaldehyde 4-phenylthiosemicarbazone, salicylaldehyde 4-methylthiosemicarbazone, $[Cr(H_2O)_6](OCOCH_3)_3$ and $[Cr(C_5H_7O_2)_3]$ were prepared as described in the literature.[10a),15,16] $[Cr(H_2O)_6]Cl_3$ and $[Cr(H_2O)_6](NO_3)_3 \cdot 3H_2O$ were commercially available and used as received without further purification. Elemental analyses were carried out with a Perkin-Elmer Series II 2400 CHNS/O analyser.

Infrared spectra were recorded on a PerkinElmer Spectrum RXI FTIR spectrometer from samples dispersed in KBr pellets (4000–400 cm^{-1} range).

Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo TGA/SDTA851[e] thermobalance using aluminium crucibles under nitrogen or oxygen stream with the heating rate of 5 °C min^{-1}. In all experiments the temperature ranged from 25 to 600 °C. The results were processed with the MettlerSTARe 9.01 software.

X-ray Diffraction Experiments

Selected crystallographic and refinement data for structures **1** and **4**, obtained by the single-crystal X-ray diffraction experiments, are reported in Table 1. The data for structures **1** and **4** were collected by ω- and φ-scans on an Oxford Xcalibur diffractometer equipped with 4-circle kappa geometry and CCD Sapphire 3

Table 2. Selected geometrical parameters (Å, °) for the compounds **1** and **4**

	1	**4**
Interatomic distances around chromium(III) ion		
Cr1–S11	2.4023(6)	2.393(2)
Cr1–S21	2.4088(7)	2.4158(18)
Cr1–O11	1.9391(16)	1.915(4)
Cr1–O21	1.9261(16)	1.922(4)
Cr1–N13	2.0286(19)	2.037(4)
Cr1–N23	2.0318(18)	2.022(4)
Bond angles around chromium(III) ion		
S11–Cr1–S21	90.58(2)	91.77(7)
S11–Cr1–O11	171.85(5)	170.89(12)
S11–Cr1–O21	94.16(5)	88.95(13)
S11–Cr1–N13	81.87(5)	82.18(12)
S11–Cr1–N23	89.08(5)	92.49(12)
S21–Cr1–O11	88.29(5)	90.89(12)
S21–Cr1–O21	171.08(5)	171.76(12)
S21–Cr1–N13	95.03(5)	92.75(11)
S21–Cr1–N23	82.84(5)	82.62(12)
O11–Cr1–O21	88.07(7)	89.67(17)
O11–Cr1–N13	90.19(7)	88.99(16)
O11–Cr1–N23	98.78(7)	96.49(16)
O21–Cr1–N13	93.12(7)	95.48(15)
O21–Cr1–N23	89.68(7)	89.15(15)
N13–Cr1–N23	170.69(7)	172.86(17)
Selected bond distances in thiosemicarbazonato ligands		
N11–C11	1.323(3)	1.333(7)
C11–S11	1.705(2)	1.686(5)
C11–N12	1.345(3)	1.342(8)
N12–N13	1.396(3)	1.387(6)
N13–C12	1.297(3)	1.292(7)
C12–C13	1.431(4)	1.423(8)
C13–C14	1.424(3)	1.439(7)
C14–O11	1.312(3)	1.310(6)
N21–C21	1.321(3)	1.326(7)
C21–S21	1.704(2)	1.708(5)
C21–N22	1.350(3)	1.337(7)
N22–N23	1.390(3)	1.388(6)
N23–C22	1.303(3)	1.294(6)
C22–C23	1.437(3)	1.418(7)
C23–C24	1.418(3)	1.425(7)
C24–O21	1.311(3)	1.310(6)
Selected torsion angles in thiosemicarbazonato ligands		
N13–N12–C11–N11	173.71(19)	176.3(5)
C11–N12–N13–C12	–164.6(2)	–162.8(5)
N12–N13–C12–C13	–179.0(2)	–177.9(5)
N23–N22–C21–N21	–179.61(17)	176.5(5)
C21–N22–N23–C22	–174.30(19)	–167.2(6)
N22–N23–C22–C23	–179.6(2)	–179.3(5)

detector and graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). For compound **1** data were acquired at 103 K under a nitrogen vapor stream, whereas for compound **4** data were collected at room temperature, 295 K. The data collection, cell refinement and data reduction, including the analytical absorption correction[17] applied for **1** and the empirical one for **4**, were performed using the CrysAlis software package.[18] Programs SHELXS-97 (Ref. 19) and SHELXL-97 (Ref. 18) integrated in the WinGX software system[20] were used to solve and refine the structures. The refinement procedure by full-matrix least squares methods based on F^2

values against all reflections included anisotropic displacement parameters for all non-H atoms. The hydrogen atoms attached to carbons were positioned geometrically and refined applying the riding model. The nitrogen (H11N, H13N, H21N and H23N in **1** and **4**) and oxygen (H1OM in **1**) bound hydrogen atoms were located in the difference Fourier maps at the final stages of refinement procedure and their coordinates were refined freely but with the restrained N−H distance of 0.88 Å for **1**, 0.86 Å for **4**, and the restrained O−H distance of 0.84 Å for **1**. For compound **4**, which crystalizes in non-centrosymmetric space-group *C c*, the absolute structure was assigned upon the Flack parameter,[21] which refined to a value of −0.10(3). The geometrical calculations and structural analyses were performed by PLATON[22] and PARST,[23] while graphics were done with ORTEP,[24] POV-Ray[25] and Mercury.[26] Main geometrical features, selected bond distances and angles, for the examined structures are summarized in Table 2.

Synthesis

General method for synthesis [Cr(Hsal 4-Metsc)2]X and [Cr(Hsal 4-Phtsc)$_2$]X X= Cl^-, NO_3^-, CH_3COO^-

The stoichiometric amount (0.85 mmol) of $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_6](NO_3)_3{\cdot}3H_2O$ and $[Cr(H_2O)_6](OCOCH_3)_3$ respectively, was added to the alcohol solution (15 mL) of salicylaldehyde 4-phenylthiosemicarbazone (H_2sal 4-Phtsc) or salicylaldehyde 4-methylthiosemicarbazone (H_2sal 4-Metsc), (0.85 mmol) and refluxed for two hours. The solution rapidly changed colour from green to dark brown. On cooling to room temperature, dark red-brown to dark brown products deposited.

The same products were isolated in substantially higher yields if chromium(III) salts were allowed to react with thiosemicarbazones in methanol in the molar ratio 1:2, respectively.

$[Cr(Hsal\ 4\text{-}Metsc)_2]Cl{\cdot}CH_3OH$ (**1**): Yield: 69 mg (15.14 %) *Anal.* Calcd. for $C_{19}H_{24}ClCrN_6O_3S_2$ (M_r = 536.02): C 42.57, H 5.51, Cl 6.61, Cr 9.70, N 15.68, S 11.96 %; found: C 42.10, H 5.76, Cl 6.54, Cr 9.80, N 15.22 %.
IR (KBr) ν_{max}/cm^{-1}: 3429 (O−H); 3133 (N^1−H), 2931 (N^2−H); 1605, 1534 (C=N); 1151 (C−O_{phen}); 912 (C=S); 713 (C−S).

$[Cr(Hsal4\text{-}Metsc)_2](NO_3)$ **(2)**: Yield: 170 mg (37.69 %) *Anal.* Calcd. for $C_{18}H_{20}CrN_7O_5S_2$ (M_r = 530.53): C 40.75, H 3.80, Cr 9.80, N 18.46, S 12.09 %; found: C 40.69, H 3.81, Cr 9.68, N 18.31, S 12.20 %.
IR (KBr) ν_{max}/cm^{-1}: 3227 (N^1−H), 2926 (N^2−H); 1601, 1559 (C=N); 1384 (NO_3); 1151 (C−O_{phen}); 917 (C=S); 756 (C−S).

$[Cr(Hsal\ 4\text{-}Metsc)_2](CH_3COO)$ (**3**): Yield: 70 mg (15.61 %) *Anal.* Calcd. for $C_{20}H_{23}CrN_6O_4S_2$ (M_r =527.57): C 45.10, H 3.76, Cr 9.70, N 11.38, S 8.81 %.
IR (KBr) ν_{max}/cm^{-1}: 3183 (N^1−H), 2901 (N^2−H); 1606, 1543 (C=N); 1471, 1441 (COO); 1201 (C−O_{phen}); 916 (C=S); 748 (C−S).

$[Cr(Hsal4\text{-}Phtsc)_2]Cl$ (**4**): Yield: 83 mg (15.54 %) *Anal.*Calcd. for $C_{28}H_{24}ClCrN_6O_2S_2$ (M_r = 628.12): C 53.55, H 3.85, Cl 5.64, Cr 8.28, N 13.38, S 10.21 %; found: C 53.49, H 3.76,Cl5.55, Cr 8.02, N 12.98, S 10.45 %.
IR (KBr) ν_{max}/cm^{-1}: 3177 (N^1−H), 2982 (N^2−H); 1605, 1569 (C=N); 1151 (C−O_{phen}); 924 (C=S); 712 (C−S).

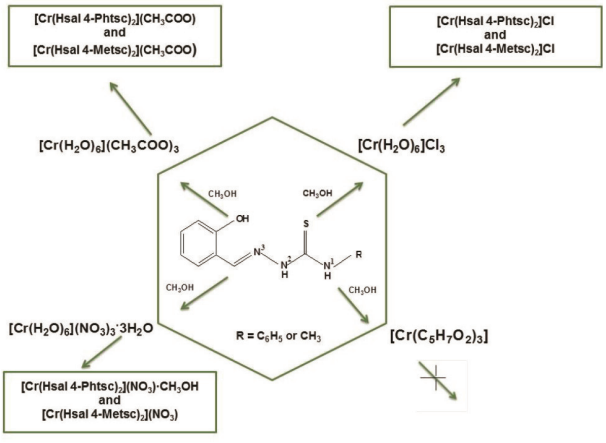
$[Cr(Hsal4\text{-}Phtsc)_2](NO_3){\cdot}CH_3OH$ (**5**) Yield: 160 mg (42.06 %) *Anal.*Calcd. for $C_{29}H_{28}CrN_7O_6S_2$ (M_r = 686.71): C 50.73, H 4.11, Cr 7.57, N 14.24, S 9.34 %; found: C 50.64, H 4.06, Cr 7.50, N 14.18, S 9.21%.
IR (KBr) ν_{max}/cm^{-1}: 3189 (N^1−H), 2901 (N^2−H); 1605, 1540 (C=N); 1384 (NO_3); 1151 (C−O_{phen}); 924 (C=S); 715 (C−S).

$[Cr(Hsal4\text{-}Phtsc)_2](CH_3COO)$ (**6**) Yield: 80 mg (14.44 %) *Anal.*Calcd. for $C_{30}H_{27}CrN_6O_4S_2$ (M_r = 651.72): C 55.29, H 4.18, Cr 7.98, N 12.89, S 9.84 %; found: C 55.18, H 4.06, Cr 7.88, N 12.44, S 9.70 %.
IR (KBr) ν_{max}/cm^{-1}: 3179 (N^1−H), 2991 (N^2−H); 1599, 1541 (C=N); 1495, 1436 (COO); 1200 (C−O_{phen}); 917 (C=S); 751 (C−S).

RESULTS AND DISCUSSION

In the course of this research, which was aimed at inspecting the chemistry of chromium(III) with potentially tridentate thiosemicarbazone ligands (H_2L), we have successfully isolated six new mononuclear complexes of the type $[Cr(HL)_2]X$ (Scheme 1).

All complexes have been prepared in a similar way, by refluxing methanol solution of chromium(III) complex salt, $[Cr(H_2O)_6]X_3$ (X = Cl, CH_3COO) or $[Cr(H_2O)_6](NO_3)_3{\cdot}3H_2O$ and appropriate thiosemicar-



Scheme 1.

bazone, regardless of the molar ratio of reactants used (1:1 or 1:2). Moreover, it should be noted that under the same conditions [$Cr(acac)_3$] has not displayed tendency to react with either ligands, even if the reaction time was prolonged to 6 hours.

IR spectroscopy can be a powerful tool for distinguishing coordination modes of the ligand, especially in the cases like here where binding of different tautomeric forms is possible. For thiosemicarbazone ligands, in this context, particularly valuable are the signals which arise from the ν(N−H) vibrations. This spectral part can be roughly divided into two subregions; one characteristic of the $\nu(N^1-H)$ vibration (above *ca* 3200 cm^{-1}), and the other of the $\nu(N^2-H)$ vibration (bellow *ca* 3200 cm^{-1}). Appearance of signals in both regions suggests that the ligand is present in the thione form, whereas the emergence of signals only in the higher energy region is indicative of the N^2-H group deprotonation.[7b] IR spectra of all complexes (**1**–**6**) display two broad bands between 2500 cm^{-1} and 3300 cm^{-1} suggesting thus the presence of ligands in the thione form. Significant shift of both ν(N−H) bands to lower wavenumbers then expected can be coupled with their involvement in extensive hydrogen bonding, as exemplified by crystal structures of compounds **1** and **4**. In the case of compounds **1** and **5**, additional bands at *ca* 3500 cm^{-1} are attributed to ν(O−H) vibrations of the solvent molecules. Intense bands which appear between 1606 cm^{-1} and 1534 cm^{-1} correspond to C=N stretching vibration and indicate the coordination of the azomethine nitrogen to chromium. For all complexes the thioamide band is found at the lower frequencies, between 923 and 912 cm^{-1}, and confirms coordination of the ligand *via* thione sulphur atom.[27] The strong bands at 1471, 1441 cm^{-1} and at 1495, 1436 cm^{-1} in spectra of complexes **3** and **6** respectively, may be attributed to COO vibration.[28] In spectra of both **2** and **5** strong band that appears at 1384 cm^{-1} is characteristic for stretching vibrations of the nitrato group.

The thermal analysis data for all complexes suggest that the ligands decompose in the temperature range from 140 to 553 °C, while the complexes **1** and **5** lose their crystallization methanol molecules in the temperature range 35–90 °C and 50–120 °C, respectively.

Crystal Structure Description

Crystallographic data for the investigated compounds **1** and **4** are summarized in Table 1. The molecular structures of compounds **1** and **4** are presented in Figure 1.

The crystal structures of both compounds contain bis(thiosemicarbazonato)chromium(III) cations, chloride anions, and additionally in the case of **1**, crystallization methanol molecules. In **1**, as well as **4**, each chromium(III) cation is coordinated by two thiosemicarbazonato ligands *via* deprotonated phenolic-oxygen O11(21), imine-nitrogen N13(23) and the sulfur S11(21) atoms (Figure 1).

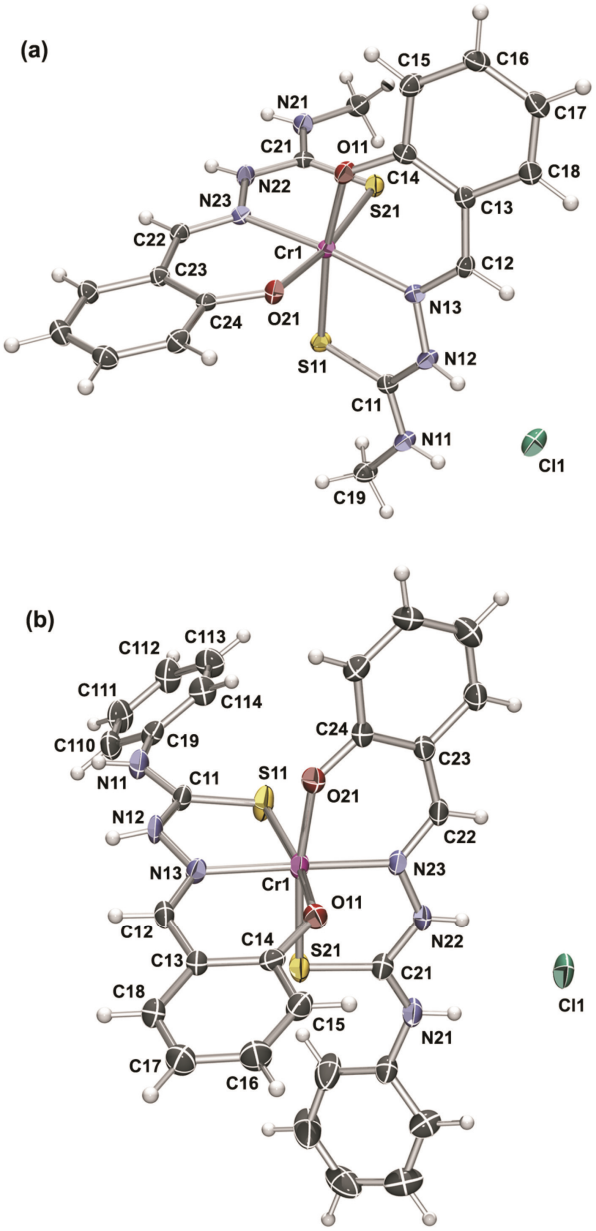


Figure 1. ORTEP,[24]-POV-Ray[25] rendered view of the compounds: (a) **1** and (b) **4** with the atom labeling schemes. The displacement ellipsoids are drawn at the 50 % probability level at 103 K for **1**, and at the 30 % probability level at 296 K for **4**. In both (a) and (b) only the first ligand ion is fully labeled, whereas for the second one only those atoms relevant for discussion are labeled. In (a) and (b) both ligands are labeled in the same way, with the atom-numbering scheme starting with 1 for the first ligand and with 2 for the second. In (a) methanol molecule is omitted for clarity.

When trying to establish in which tautomeric form, thione or thiole, ligands coordinate to a metal

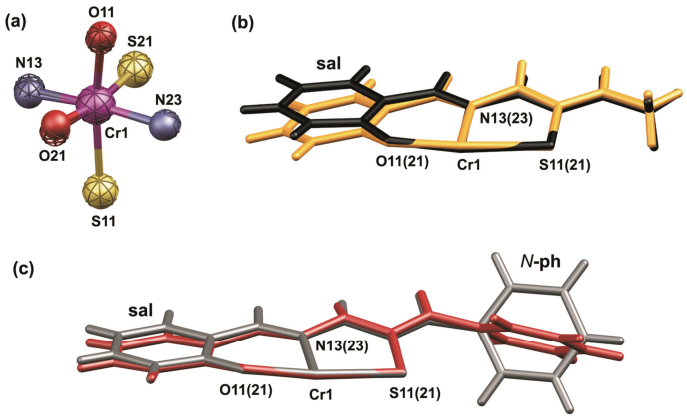


Figure 2. (a) Comparison of the primary coordination sphere geometries for bis(thiosemicarbazonato)chromium(III) cations of **1** and **4**. For **1**, atoms are presented as solid spheres, and for **4** as wireframe spheres. The diagram was constructed by overlapping Cr1 ions. (b) Overlapping diagram for the two coordinated ligands in **1**; the first ligand molecule (the atom-numbering starting with 1, see Figure 1(a)) is colored yellow and the second one black. The diagram was constructed by overlapping Cr1, O11(21), S11(21) and N13(23) atoms. Dihedral angle between the planes of salicylidene rings is *ca* 10.4°. (b) Overlapping diagram for the two coordinated ligands in **4**; the first ligand molecule (the atom-numbering starting with 1, see Figure 1(b)) is colored red and the second one gray. The diagram was constructed by overlapping Cr1, O11(21), S11(21) and N13(23) atoms. Dihedral angle between the planes of **sal** rings is *ca* 5.6°, while the one between the planes of *N*-phenyl rings (denoted as ***N*-ph**) is *ca* 83.0°.

cation, bond distances of those structural parts which get mostly affected by the change of tautomeric should be taken as a key parameter. For here examined structures, those bonds are C11(21)–S11(21) and C11(21)–N12(22). Based on the careful structural analysis and the comparison of specific bond length values with the ones characteristic for thiole and thione form, established through CSD search,[29,30] it can be unambiguously concluded that in both compounds ligands coordinate to chromium(III) ions exclusively in their thione form.

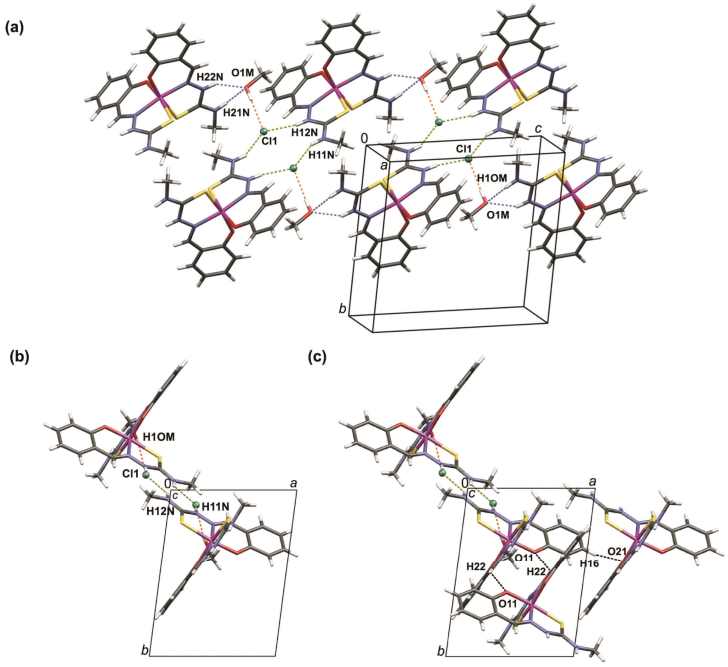


Figure 3. Crystal packing in **1** showing: (a) infinite double chain, consisting of bis(4-methyl thiosemicarbazonato)chromium(III) cations, chloride anions and methanol molecules spreads along the *c*-axis. Chain is assembled *via* N–H···O (presented by blue dashed lines) and charge assisted O–H···Cl (presented by orange dashed lines) and N–H···Cl (presented by green dashed lines) hydrogen bonds (Table 3). (b) View on the chain down the *c*-axis. In (a) and (b) exactly the same chain is presented. (c) Chains are further associated through C16–H16···O21 and C22–H22···O11 interactions (both are presented by black dashed lines). Chains are viewed down the *c*-axis.

Table 3. Hydrogen bond geometry (Å,°) for compounds **1** and **4**

D–H···A	D–H	H···A	D···A	∠D–H···A	Symmetry code
		1			
O1M–H1OM···Cl1	0.83(3)	2.25(3)	3.074(2)	170(3)	–
N11–H11N···Cl1	0.86(2)	2.57(2)	3.281(2)	140(2)	–*x*, –*y*, 1–*z*
N12–H12N···Cl1	0.85(2)	2.25(2)	3.085(2)	170(2)	–
N21–H21N···O1M	0.84(2)	2.13(2)	2.862(3)	147(2)	*x*, *y*, –1+*z*
N22–H22N···O1M	0.85(2)	2.05(2)	2.802(3)	146(2)	*x*, *y*, –1+*z*
C16–H16···O21	0.9500	2.5800	3.385(3)	142.00	1+*x*, *y*, *z*
C22–H22···O11	0.9500	2.4600	3.238(3)	139.00	1–*x*, 1–*y*, –*z*
		4			
N11–H11N···Cl1	0.85(3)	2.39(5)	3.150(5)	149(5)	*x*, –1+*y*, *z*
N12–H12N···Cl1	0.85(4)	2.35(4)	3.124(5)	152(5)	*x*, –1+*y*, *z*
N21–H21N···Cl1	0.85(3)	2.40(4)	3.191(5)	155(5)	–
N22–H22N···Cl1	0.85(3)	2.33(2)	3.122(4)	154(5)	–
C210–H210···S11	0.9300	2.7000	3.465(7)	140.00	*x*, 1–*y*, 1/2+*z*
C28–H28···O11	0.9300	2.637(3)	3.427(7)	143.23(35)	*x*, –*y*+1, *z*–1/2
C18–H18···O21	0.9300	2.610(4)	3.513(6)	163.96(34)	*x*, –*y*, *z*+1/2

Coordination of the ligands through *O, N* and *S* donor atoms creates distorted octahedral environment around each chromium(III) ion with *cis* positioned *S* and *O* atoms of the two ligands (Figures 1 and 2(a)). Consequently, such arrangement sets the two imine *N* atoms in mutual *trans* position (Figures 1 and 2(a)). The distortion from ideal octahedral geometry is nearly the same for both complexes (Figure 2(a)), and is best illustrated by divergent bond lengths and angles around the central chromium ion (Table 2). As expected, within the same complex, the equivalent bond lengths of the coordinated ligands do not diverge significantly, but conformations of the two ligands show interesting dissimilarities. For **1**, the largest disparity is observed in the arrangement of salicylidene rings as a cumulative result of differences in torsion angles along the ligands' backbones (Figure 2(b), Table 2). In **4**, these differences are more subtle, whereas the most obvious dissimilarity is in the arrangement of terminal *N*-phenyl rings (Figure 2(c)).

Due to the presence of solvent methanol molecules in **1**, primary supramolecular architectures of **1** and **4** differ deeply. In **1**, bis(salicylaldehyde 4-methylthiosemicarbazonato)chromium(III) cations, chloride anions and methanol molecules associate *via* intermolecular N−H···O, and charge assisted O−H···Cl and N−H···Cl hydrogen bonds to form double chains, which spread along the *c*-axis (Figure 3(a) and Table 3). Very interesting in this structure is that each of the two coordinated ligands employs its N−H functionalities in different hydrogen bonding motifs, which can be easily described in terms of graph set notation. Whereas one ligand uses its N−H groups to bind chloride anions forming thus a $R_4^2(12)$ pattern, the second one employs them to bind methanol oxygen in a tweezer-like manner, creating subsequently $R_2^1(6)$ motif (Figure 3(a) and (b), Table 3). Finally, each chloride anion participates in an additional O−H···Cl hydrogen bond with $D_1^1(2)$ motif. Chains assembled in such manner further associate through C16−H16···O21 interactions along the *a*-axis, and C22−H22···O11 down the *b*-axis into the final three-dimensional architecture (Figure 3(c), Table 3). In contrast to the structure of **1**, in **4** each ligand uses its N−H functionalities in the same way, *i.e.* to bind chloride anions in a tweezer-like fashion, producing thus a double $R_2^1(6)$ motif (Figure 4(a) and Table 3). Such hydrogen bonding pattern allows growth of supramolecular chains along the *b*-axis. The chains are then associated through C−H···O and C−H···S interactions into layers in the *bc* plane (Figure 4(b) and (c), Table 3). The layers are finally stacked *via* van der Waals interactions along the *a*-axis into three-dimensional architecture.

CONCLUSION

Series of novel octahedral chromium(III) complexes of the general formula $[Cr(HL)_2]X$ (X = Cl^-, NO_3^- and CH_3COO^-) was successfully prepared by the reaction of thiosemicarbazone ligands (salicylaldehyde 4-methylthiosemicarbazone and salicylaldehyde 4-phenylthiosemicarbazone) with assorted chromium(III) salts. In contrast, routes employing $[Cr(acac)_3]$ as a starting material proved ineffective for the synthesis of the corresponding thiosemicarbazonato complexes. The X-ray crystallographic studies for compounds **1** and **4**, combined with IR spectral data revealed that in all iso-

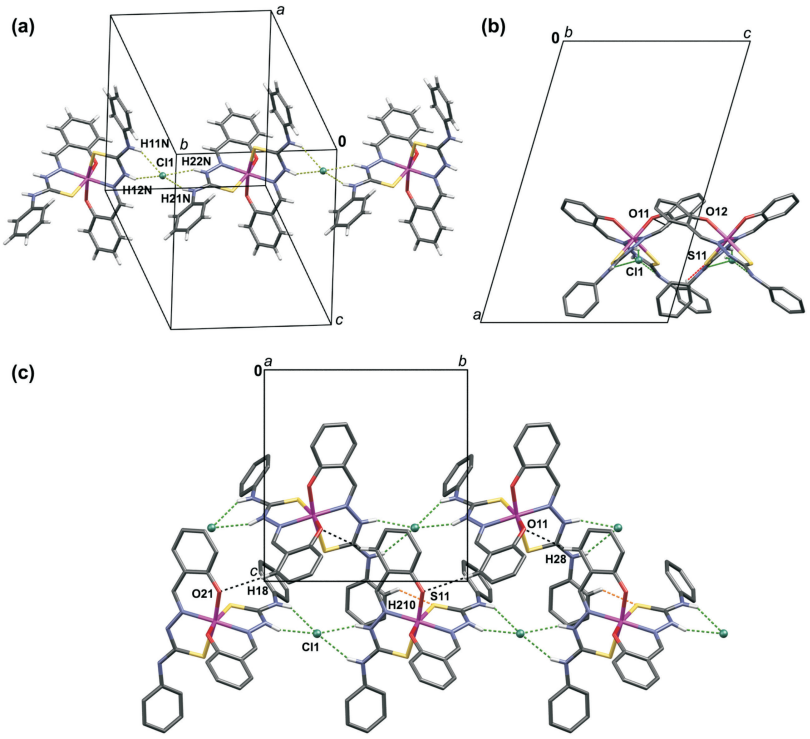


Figure 4. Crystal packing in **4** showing: (a) infinite chain consisting of bis(4-phenyl thiosemicarbazonato)chromium(III) cations and chloride anions which spreads along the *b*-axis. Chain is assembled *via* charge assisted N–H···Cl hydrogen bonds (presented by green dashed lines). (b) And (c) chains are further associated through C18–H18···O21 and C28–H28···O11 (presented by black dashed line) and C210–H210···S11(presented by orange dashed line) interactions into layers in the *bc* plane. In (b) chains are viewed down the *b*-axis and in (c) down the *a*-axis. In (b) and (c) exactly the same chains are presented.

lated complexes thiosemicarbazone ligands coordinate in their thione form, as singly charged anions through *O,N,S* donor atoms. The X-ray diffraction studies on **1** and **4** have in addition revealed several interesting structural features of these complexes; similar distortion of the octahedral geometry, inequivalent conformation of the two ligands within the same complex, and due to the presence of crystallization methanol molecules in **1**, exceedingly richer pattern of hydrogen bonds. Finally, the results of this study in combination with previously reported examples, indicate that the family of salicylaldehyde thiosemicarbazones has the preference for binding to chromium(III) exclusively in their thione form.

Supplementary Materials. – Supplementary crystallographic data sets for the structures of **1** and **4** are available through the Cambridge Structural Data base with deposition numbers 892669 (for **1**) and 892670 (for **4**). Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336 033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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30. The search was performed on the family of thiosemicarbazones derived from salicylaldehyde and its derivatives which are coordinated to any transition metal in O,N,S manner. For the ligand present in the thione form, C1=S1 and C1−N2 bonds are expected (for numeration see Scheme 1). In contrast, for the ligand present in the thiole form, the same bonds should be present as C−S and C=N. The search criteria used for the ligand coordinated in the thione form was molecular diagram involving any transition metal bound to thiosemicarbazone through phenolic oxygen, imino nitrogen and sulphur, allowing C1−S1 and C1−N2 to posses any bond character, but requiring the presence of hydrogen at N2 atom. For the ligand coordinated in the thione form 28 entries were found, with altogether 39 structural fragments (repeated determinations were removed manually from the count). Analysis of C−S distance reveals that in for the thione form its value ranges from 1.668 Å to 1.742 Å with the mean value of 1.707 Å. In the same population, C1−N2 distance ranges from 1.287 Å to 1.362 Å and with the mean value of 1.330 Å. The search criteria used for the ligand coordinated in the thiole form was molecular diagram involving any transition metal bound to thiosemicarbazone through phenolic oxygen, imino nitrogen and sulphur, allowing C1−S1 to posses any bond character, but requiring double bond between C1 and N2 atoms without hydrogen atom present at N2. For the ligand coordinated in the thiole form 134 entries were found, with 174 structural fragments (repeated determinations were removed manually from the count). In addition, 2 entries (2 fragments) were discarded due to unrealistically short C−S distance and the analysis was performed with the remaining ones (172 fragments). For the thiole form, C−S distance ranges from 1.706 Å to 1.812 Å with the mean value of 1.749 Å. In the same set, C1−N2 distance ranges from 1.271 Å to 1.332 Å and with the mean value of 1.302 Å.