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Synthesis, structures and magnetic properties of octahedral Co(III) complexes of heteroaromatic hydrazones with tetrakisothiocyanato Co(II) anions

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Abstract

Octahedral Co(III) complexes with heteroaromatic hydrazones ((*E*)-*N,N,N*-trimethyl-2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)ethan-1-aminium chloride and (*E*)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide) and tetrakisothiocyanato Co(II) complex anions have been synthesized, characterized by elemental analysis, IR and NMR spectroscopy, single-crystal X-ray diffraction and magnetic measurements. NMR spectroscopy showed that octahedral Co(III) complex cations of both compounds are stable in DMSO solution. Measured effective magnetic moments, which completely originates from complex anion $[\text{Co}(\text{NCS})_4]^{2-}$ are practically constant and very close to the expected value for Co^{2+} ion with spin $S = 3/2$ and completely quenched orbital angular momentum. Co(III) ions in octahedral complex cations are in a low spin magnetic state with $S = 0$ and do not contribute to the magnetic signal.

Keywords: Thiocyanate, hydrazones, Co(III) and Co(II) complexes, X-ray, magnetic properties

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1. Introduction

There is a considerable interest in design and synthesis of Schiff bases complexes containing pseudohalide ligands due to their structural diversity, magnetic and spectral properties, as well as biological activity [1–12]. Thiocyanate is an ambidentate pseudohalide ligand, which can be coordinated through nitrogen or sulfur donor atom as monodentate or as a bridge between metal centers [13]. In some cases monodentately coordinated thiocyanate ligands can participate in intermolecular hydrogen bonding between metal complexes having significant influence on their stability in solid state [14,15]. Girard's reagents (Girard's T (trimethylacetylhydrazide ammonium chloride), Girard's D (N,N-dimethylglycine hydrazide hydrochloride), Girard's P (pyridinioacetohydrazide chloride)) are N-substituted glycine hydrazides, which are mostly used in analytical chemistry for separation of carbonyl compounds from complex organic mixtures [16]. The reaction of Girard's reagents with carbonyl group gives water soluble hydrazones. Metal complexes of Girard's reagents hydrazones have not been extensively studied. Among them, the mostly investigated are metal complexes of Girard's T hydrazones. The Girard's T reagent hydrazones exhibit keto-enol tautomerism and can coordinate metal ions in non-deprotonated positively charged form or deprotonated formally neutral zwitter-ionic form. The presence of the quaternary ammonium group in the metal complexes of Girard's T reagent hydrazones improves their water solubility and has effect on their biological activity [11]. Heteroaromatic pyridine and thiazole rings are privileged scaffold in medicinal chemistry, which are present in a large number of compounds possessing antimicrobial and antitumor activity [17,18]. Although, many thiosemicarbazone-based ligands and their metal complexes were intensively studied due to their interesting structures and potential applications [19], there are only few reported metal complexes with thiosemicarbazone-based five-membered heterocycles [20–26]. Among the other possible applications, some thiosemicarbazone based ligands are used for synthesis of Fe(III) spin-crossover (SCO) systems [23–28]. From the magnetochemistry point of view, Co(II) compounds are of importance for design of molecule based magnetic materials. Spin crossover (SCO) is expected to occur in octahedral complexes of first-row transition metal ions with 4–7 3d valence electrons. In such complexes metal ions can exist in several spin states, and small energy difference between these states allow certain stimuli (light, heat, or pressure) to induce reversible switching of the predominant populations of two states. The majority of known cobalt(II) SCO systems are six-coordinate compounds involving thermally induced spin

transition. Such changes of spin state are also observed for four-coordinate and some five-coordinate complexes [29].

All these facts motivate us to perform reaction of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and heteroaromatic hydrazones (**HL**¹Cl (*E*)-*N,N,N*-trimethyl-2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)ethan-1-aminium-chloride and **HL**² (*E*)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide) in the presence of excess of thiocyanate anions and study the structure and magnetic properties of obtained compounds. In the present work, the synthesis and characterization of obtained octahedral Co(III) complexes with heteroaromatic hydrazones (**HL**¹Cl and **HL**²) and tetrakis(thiocyanato) Co(II) complex anions are reported.

2. Experimental

2.1. Materials and methods

2-Acetylpyridine ($\geq 99\%$), 2-acetylthiazole (99%), Girard's T reagent (99%) and thiosemicarbazide (99%) were obtained from Sigma-Aldrich. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer using the ATR technique in the region $4000\text{--}400\text{ cm}^{-1}$ (vs-very strong, s-strong, m-medium, w-weak, bs - broad signal). ¹H and ¹³C NMR spectra were recorded on Bruker Avance 500 spectrometer (¹H at 500 MHz; ¹³C at 125 MHz) at room temperature using TMS as internal standard in DMSO-d₆ (numbering of atoms according scheme 1). Chemical shifts are expressed in ppm (δ) values and coupling constants (*J*) in Hz. Elemental analyses (C, H, and N) were performed by standard micro-methods using the ELEMENTARVario ELIII C.H.N.S.O analyzer. An Agilent 6224 time-of-flight (TOF) mass spectrometer equipped with a double orthogonal electrospray source at atmospheric pressure ionization (ESI) coupled to an Agilent 1260 HPLC was used for recording HRMS spectra. Mobile phase composed of two solvents: A was 0.1% formic acid in Milli-Q water, and B was 0.1% formic acid in acetonitrile mixed in the ratio of 1:1. Compound was prepared by dissolving the sample in acetonitrile and injected (0.1 μL) into the LC-MS. Flow rate was 0.4 mL/min. Fragmentor voltage was 150 V. Capillary voltage 4000 V.

2.2. Synthesis

2.2.1. Synthesis of ligand **HL¹Cl** (*E*)-*N,N,N*-trimethyl-2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)ethan-1-aminium-chloride

The ligand **HL¹Cl** was synthesized in the reaction of Girard's T reagent (1.676 g, 1.00 mmol) and 2-acetylpyridine (1.120 mL, 1.00 mmol) in methanol (50 mL). The reaction mixture was acidified with 3–4 drop of 2M HCl and refluxed for 120 minutes at 85 °C. The ligand was obtained as a white solid after evaporation of reaction solution at room temperature (~ 20 °C) during 5 days. Yield 87%. IR: 3387 (w), 3127 (m), 3090 (m), 3049 (m), 3016 (m), 2950 (s), 1700 (vs), 1612 (w), 1549 (s), 1485 (m), 1400 (m), 1300 (w), 1253 (w), 1200 (s), 1153 (w), 1135 (m), 1095 (w), 1073 (m), 975 (w), 944 (w), 914 (m), 748 (w), 683 (w).

Elemental analysis calcd for C₁₂H₁₉ClN₄O: N 20.69 %, C 53.23 %, H 7.07 %, found: N 20.49 %, C 53.34 %, H 7.38 %.

¹H NMR: 11.41 (N-H, s), 4.92 (C10-H₂, s), 3.35 (C11-H₉, s), 2.37 (C8-H₃, s), 8.62 (C3-H, m), 7.45 (C4-H, m), 7.91 (C5-H, td, *J*³ = 10 Hz, *J*⁴ = 5 Hz), 8.12 (C6-H, d, *J*³ = 10 Hz)

¹³C NMR: 63.2 (C10), 53.7 (C11), 13.9 (C8), 149.2 (C3), 124.9 (C4), 137.2 (C5), 120.8 (C6), 154.9 (C7), 155.3 (C2), 167.1 (C9).

2.2.2. Synthesis of ligand **HL²** (*E*)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide

The ligand **HL²** was synthesized in the reaction of thiosemicarbazide (0.911 g, 1.00 mmol) and 2-acetylthiazole (1.040 mL, 1.00 mmol) in water (20 mL). The reaction mixture was acidified with 3 drops of 2M HCl and refluxed for 180 minutes at 85 °C. White precipitate was formed during reaction. The solid was washed with cold water and filtered. Yield 91%. IR: 3436 (s), 3248 (s), 3188 (s), 3099 (m), 3071 (m), 2983 (m), 2066 (w), 1648 (w), 1589 (s), 1510 (s), 1482 (s), 1452 (m), 1425 (s), 1365 (m), 1282 (m), 1166 (m), 1107 (m), 1069 (m), 1039 (m), 958 (w), 881 (w), 847 (w), 755 (w), 712 (w), 638 (w).

Elemental analysis calcd for C₆H₈N₄S₂: N 27.98 %, C 35.98 %, H 4.03 %, S 32.02 %, found: N 27.88 %, C 35.74 %, H 4.26 %, S 31.98 %.

^1H NMR: 7.89 (C4-H, d $J^3 = 5$ Hz), 7.80 (C5-H, d, $J^3 = 5$ Hz), 2.43 (C7-H₃, s), 10.67 (N-H, s), 8.53 and 7.69 (N-H₂, bs).

^{13}C NMR: 14.1 (C7), 144.7 (C2), 179.4 (C8), 167.5 (C6), 143.7 (C4), 123.1 (C5).

2.2.3. Synthesis of $[\text{CoL}^1]_2[\text{Co}(\text{NCS})_4]\text{BF}_4$ complex (**1**)

Into the solution of ligand **HL**¹Cl (54 mg, 0.20 mmol) in methanol (20 mL), $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (80 mg, 0.23 mmol) dissolved in methanol (5 mL) was added. After 30 minutes the solution of NH_4SCN (55 mg, 0.72 mmol) in methanol (5 mL) was added into reaction mixture. Reaction mixture was stirred with heating for 3 h at 55 °C. Green crystals suitable for X-ray analysis arose from the reaction solution after slow evaporation of solvent in refrigerator (~ 7 °C) during two weeks. IR: 3080 (w), 3032 (w), 2065 (vs), 1623 (w), 1603 (w), 1566 (w), 1520 (s), 1466 (m), 1442 (m), 1397 (m), 1375 (m), 1339 (w), 1313 (m), 1265 (w), 1237 (w), 1206 (w), 1152 (w), 1053 (s), 972 (w), 923(w), 766 (w).

Elemental analysis calcd for $\text{C}_{28}\text{H}_{36}\text{BCo}_2\text{F}_4\text{N}_{12}\text{O}_2\text{S}_4$: N 18.56 %, C 37.14 %, H 4.01 %, S 14.16 %, found: N 19.14 %, C 37.43 %, H 4.09 %, S 14.07 %.

HMRS (ESI⁺): m/z calcd for $\text{C}_{24}\text{H}_{36}\text{BCo}^{\text{II}}\text{F}_4\text{N}_8\text{O}_2^+$ [$\text{M} + \text{e}^- - \text{Co}(\text{NCS})_4^{2-}$]⁺, 613.2353; found, 613.2349 (**Fig. S1**).

^1H NMR: 4.28 (C10-H₂, s), 3.03 (C11-H₉, s), 3.32 (C8-H₃, s), 8.01 (C3-H, d, $J^3 = 5$ Hz), 7.59 (C4-H, q, $J^3 = 5$ Hz), 8.27 (C5-H, C6-H, d $J^3 = 5$ Hz)

^{13}C NMR: 62.4 (C10), 53.8 (C11), 16.1 (C8), 153.4 (C3), 130.3 (C4), 128.1 (C5), 142.9 (C6), 167.8 (C7), 159.9 (C2), 177.7 (C9).

2.2.4. Synthesis of $[\text{CoL}^2]_2[\text{Co}(\text{NCS})_4] \cdot 2\text{H}_2\text{O}$ complex (**2**)

Into the solution of ligand **HL**² (40 mg, 0.20 mmol) in methanol (15 mL), $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (70 mg, 0.21 mmol) dissolved in methanol (5 mL) and solid NH_4SCN (38 mg, 0.50 mmol) were added. Reaction mixture was stirred with heating for 3 h at 55 °C. Green crystals suitable for X-ray analysis arose from the reaction solution after slow evaporation of solvent in refrigerator (~ 7°C) during ten days. IR: 3642 (w), 3625 (w), 3565 (w), 3544 (w), 3282 (s), 3109 (s), 2060 (s),

1653 (m), 1612 (m), 1548 (m), 1503 (m), 1462 (s), 1438 (s), 1384 (s), 1341 (s), 1297 (s), 1208 (s), 1164 (s), 1132 (m), 1068 (m), 1029 (m), 893 (m), 799 (w), 738 (w), 681 (w), 651 (w).

Elemental analysis calcd for $C_{28}H_{32}Co_3N_{20}O_2S_{12}$: N 22.55%, C 27.07 %, H 2.60 %, S 30.97 %, found: N 22.74 %, C 27.33 %, H 2.59 %, S 30.77 %.

HMRS (ESI+): m/z calcd for $C_{12}H_{14}CoN_8S_4^+ [M - CoL_2^+ - Co(NCS)_4^{2-} - 2H_2O]^+$, 456.9551; found, 456.9547; L = $C_6H_7N_4S_2$ (**Fig. S2**).

1H NMR: 7.51 (C4-H, d, $J^3 = 5$ Hz), 7.98 (C5-H, d, $J^3 = 5$ Hz) 2.74 (C7-H₃, s) 8.03 (N-H₂, bs)

^{13}C NMR: 16.6 (C7), 149.0 (C2), 181.6 (C8), 167.8 (C6), 140.4 (C4), 125.3 (C5).

2.3. X-ray Crystallography

The molecular structures of complexes **1** and **2** were determined by single-crystal X-ray diffraction methods. Crystallographic data and refinement details are given in Table 1. Diffraction data were collected at room temperature with Agilent SuperNova dual source diffractometer using an Atlas detector and equipped with mirror-monochromated MoK α radiation ($\lambda = 0.71073$ Å). The data were processed by using CrysAlis PRO [30]. The structures were solved using SHELXT [31]. All the structures were refined against F^2 on all data by full-matrix least-squares with SHELXL-2016 [32]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms are fixed by using a riding model and treated isotropically with the program package OLEX2 [33]. Flack parameter was refined and determined since the space group is chiral P21212 (no.18) and since the chemical composition of the crystal (presence of heavier atoms Co, S...) is such that the effects of anomalous dispersion enable the determination of absolute structure. Unfortunately the final Flack parameter is not 0 (or 1 which would require that the structure should be inverted) – it is 0.478(16) which means that the crystal was racemic twin.

It's important to emphasize two things:

1. that diffraction pattern strongly supports the acentric space group P21212 (it is in accordance with systematically absent reflections, e-statistics test support the non-centrosymmetric structure, agreement among symmetry equivalent reflections)

2. testing programs (checkCIF, Platon) don't report higher symmetry, visual inspection of our asymmetric unit also exclude the presence of inversion or reflection symmetry within it.

In spite of that, to be sure that there are no other symmetry elements present within the structure (inversion, mirror or glide planes) which would cause that the structure is racemic, we performed structure determination in higher symmetries (supergroups of P21212, which are achiral and correspond to »racemic structures«). We did not obtain any reasonable structure solution in such higher symmetries.

The conclusion is that the value of Flack parameter of 0.478(16) is due to the racemic twinning.

<Table 1>

2.4. Magnetic Properties

Magnetic properties were investigated on polynuclear samples using a Quantum Design MPMS-XL-5 SQUID magnetometer. Susceptibility has been measured between 2 K and 300 K in a constant magnetic field of 1 kOe. All presented data are corrected for temperature independent diamagnetic contribution of sample holder and inner shell electrons according to the Pascal's tables [34].

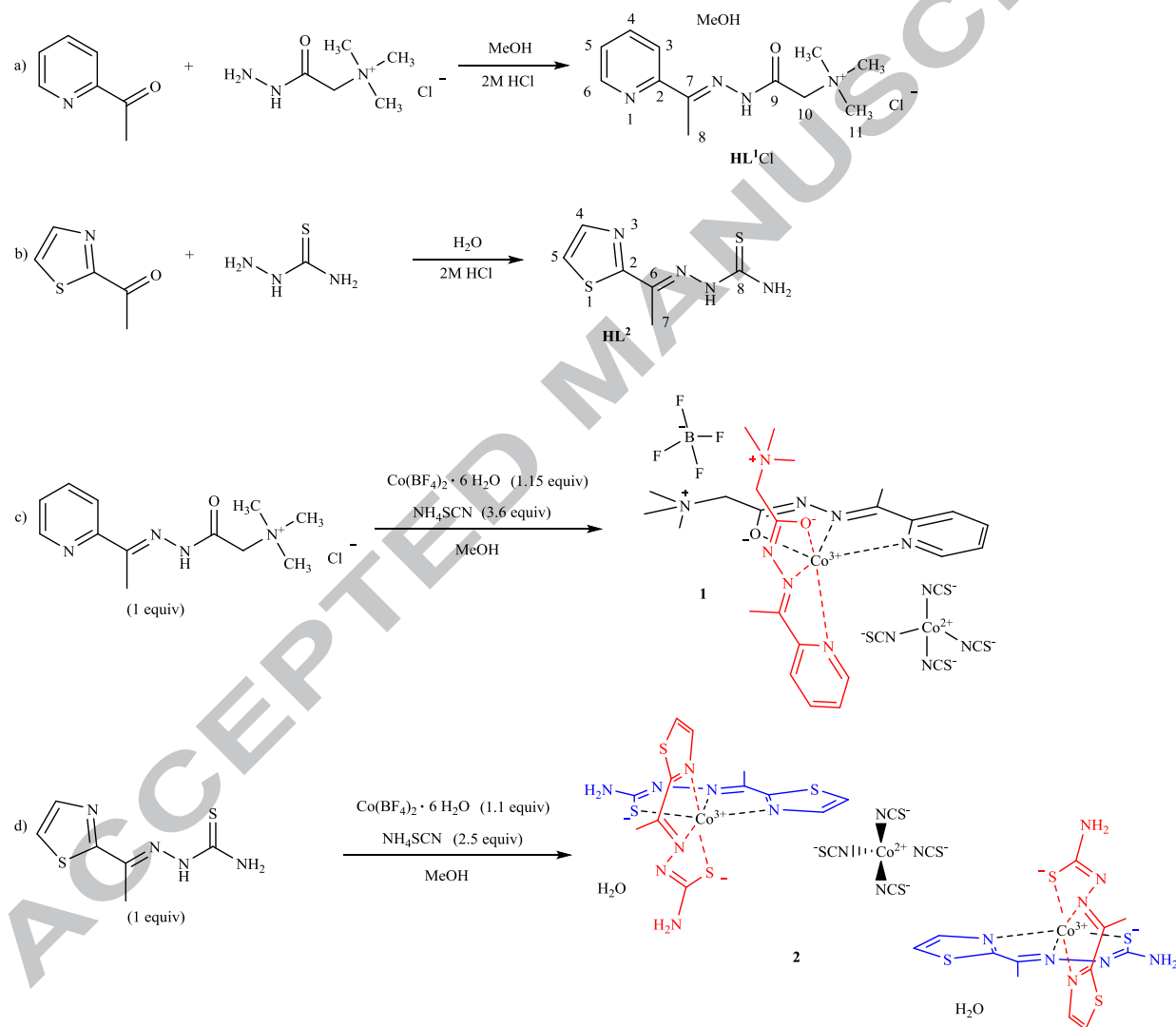
3. Results and discussion

3.1. Synthesis

The ligand (*E*)-*N,N,N*-trimethyl-2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)ethan-1-aminiumchloride (**HL**¹Cl), Scheme 1a, was obtained as described previously [15]. The novel ligand (*E*)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide (**HL**²), Scheme 1b, was obtained in the condensation reaction of thiosemicarbazide and 2-acetylthiazole in water. Reaction of the ligand **HL**¹Cl with Co(BF₄)₂·6H₂O and NH₄SCN in molar ratio 1 : 1.15 : 3.6 in methanol gives compound **1** with composition [CoL¹₂][Co(NCS)₄]BF₄, Scheme 1c. In octahedral complex cation of compound **1** two molecules of deprotonated hydrazone ligand are coordinated

through pyridine nitrogen, azomethine nitrogen and carbonyl oxygen atoms with Co(III) metal center. Compound **1** possesses two anions, tetrahedral isothiocyanato Co(II) complex and BF_4^- .

In the reaction of HL^2 with $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and NH_4SCN in molar ratio 1 : 1.1 : 2.5 in methanol, compound (**2**) with composition $[\text{CoL}^2_2]_2[\text{Co}(\text{NCS})_4] \cdot 2\text{H}_2\text{O}$ was obtained, Scheme 1d. Two octahedral Co(III) complex cations in compound **2** are formed by coordination of deprotonated hydrazone ligands through pyridine nitrogen, azomethine nitrogen and sulfur atom. Co(II) complex anion in compound **2** is the same as in compound **1**.



Scheme 1. Synthesis of ligands (HL^1Cl and HL^2) and complexes **1** and **2**

3.2. IR Spectroscopy

In complex **1** the hydrazone ligand is coordinated in deprotonated form since the vibration of $\nu(\text{N-H})$ at 3387 cm^{-1} observed in the spectrum of HL^1Cl is absent in the spectrum of complex **1**. In the IR spectrum of complex **1** a band at 1623 cm^{-1} corresponding to $\nu(\text{O}^--\text{C}=\text{N})$ vibration of deprotonated α -oxyazine form of ligand appeared instead of the carbonyl group band of noncoordinated HL^1Cl at 1700 cm^{-1} . The coordination of azomethine nitrogen produced a shift of $\nu(\text{C}=\text{N})$ from 1612 cm^{-1} in the spectrum of HL^1Cl to 1603 cm^{-1} in the spectrum of **1**.

In the spectrum of complex **1** strong band at 2065 cm^{-1} corresponds to the SCN^- group coordinated through nitrogen atom. A strong band at 1053 cm^{-1} confirms the presence of BF_4^- anion in **1**.

In the IR spectrum of complex **2** bands at 1341 and 893 cm^{-1} corresponds to $\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S}) + \gamma(\text{CH})$, respectively, while in the spectrum of noncoordinated HL^2 ligand $\nu(\text{C}=\text{S}) + \nu(\text{C}=\text{N})$ and $\nu(\text{C}=\text{S}) + \gamma(\text{CH})$ bands appeared at 1365 and 847 cm^{-1} .

The coordination of azomethine nitrogen results in shift of $\nu(\text{C}=\text{N})$ from 1589 cm^{-1} in the spectrum of HL^2 to 1612 cm^{-1} in the spectrum of complex **2**. In the spectrum of complex **2** strong band at 2060 cm^{-1} can be attributed to the SCN^- group coordinated through nitrogen atom.

3.3. NMR Spectroscopy

Complex cations of both compounds **1** and **2** are stable in DMSO solution and their structures correspond to the structures determined in solid state. The signal of NH group of HL^1Cl hydrazone ligand observed at 11.41 ppm in its ^1H NMR spectrum is absent in the spectrum of complex **1**. Coordination of carbonyl group results in upfield shift of neighboring methylene group ($\text{C}10\text{-H}_2$) protons from 4.92 ppm in the spectrum of ligand to 4.28 ppm in the spectrum of complex **1**. Also, protons of methyl group $\text{C}8\text{-H}_3$ are shifted downfield due to coordination of azomethine nitrogen (2.37 ppm in the spectrum of HL^1Cl and 3.32 ppm in the spectrum of **1**).

Coordination of carbonyl oxygen atom shifts the signal of $\text{C}9$ strongly downfield from 167.1 ppm in ^{13}C NMR spectrum of HL^1Cl to 177.7 ppm in the spectrum of complex **1**. Due to coordination of pyridine nitrogen atom the signals of the most of carbon atoms from pyridine ring are shifted downfield. Also, downfield shift is observed for signal of azomethine carbon atom $\text{C}7$ (154.9 ppm in the spectrum of HL^1Cl and 167.8 ppm in the spectrum of complex **1**).

Similar situation is observed for **HL**² ligand and complex **2**. The signal of NH group is absent in the spectrum of **2**. Coordination of thiazole nitrogen atom results in shifts of all thiazole atoms signal in the spectrum of **2**. Downfield shift is observed for the signals of methyl carbon atom C7 (14.1 ppm in the spectrum of **HL**² and 16.6 ppm in the spectrum of **2**) and C8 (179.4 ppm in the spectrum of **HL**² and 181.6 ppm in the spectrum of **2**). The signal of azomethine nitrogen C6 is slightly shifted downfield upon coordination (from 167.5 ppm in the spectrum of **HL**² to 167.8 ppm in the spectrum of **2**).

3.4. Crystal structures

X-ray crystal structures of **1** and **2** with atom numbering schemes are presented in **Figs. 1** and **2**, respectively. Selected bond lengths and bond angles for complexes **1** and **2** are listed in **Table 1**. The complex **1** crystallizes in the monoclinic space group *P2₁/c*. The asymmetric unit of **1** consists of [CoL¹₂]³⁺ complex cation, [Co(NCS)₄]²⁻ complex anion and BF₄⁻. In the [CoL¹₂]³⁺ complex cation two ligand molecules **L**¹ in a zwitter ionic form coordinate the central metal ion in a *mer* arrangement, forming an octahedral complex by chelation through two NNO sets of donor atoms. Each ligand molecule coordinates to metallic center through pyridyl nitrogen, imine nitrogen and enolate oxygen atoms. Co-N_{py} [Co1-N1 1.917(4) Å, Co1-N5 1.926(4) Å, Co-N_{py} (mean value) 1.922 Å], Co-N_{imine} [Co1-N2 1.853(3) Å, Co1-N6 1.853(4) Å, Co-N_{imine} (mean value) 1.853 Å] and Co-O_{enolate} [Co1-O1 1.903(3) Å, Co1-O2 1.909(3) Å, Co-O_{enolate} (mean value) 1.906 Å] bond lengths (**Table 1**) are comparable to those observed in reported octahedral Co(III)-N₄O₂ complexes with hydrazone based ligands [35–43] (**Table S1**). The tridentate coordination of each ligand molecule implies the formation of two fused five-membered chelate rings (Co-N-C-C-N and Co-N-N-C-O). The chelate rings Co-N-C-C-N and Co-N-N-C-O are nearly coplanar, as indicated by the dihedral angles of 1.8° and 1.4° for the rings fused along Co1-N2 and Co1-N6 bonds, respectively. The two chelation planes, comprising the atoms O-N-N-Co are almost perpendicular, as indicated by the dihedral angle of 87.2°. One of the measures of the octahedral strain is average ΔO_h value, defined as the mean deviation of 12 octahedral angles from ideal 90°. The distorted octahedron formed around Co1 in **1** exhibits average ΔO_h value of 5.5°. The non-classical hydrogen bonds of C-H...F type [44] which operate between complex cation [CoL¹₂]³⁺ and BF₄⁻ anions (**Table 2**) generate chains parallel with the [010] direction (**Fig. 3**). Two methyl groups from the same ligand molecule and one methylene group

from the other ligand molecule serve as hydrogen bond donors. The methyl group C22 is donor to F1 and F3 and C19 is donor to F4 at $x, -1+y, z$. The methylene group C9 is hydrogen bond donor to F1 which serves as double acceptor. No classic hydrogen bonds have been found in crystals of **1**.

The complex **2** crystallizes in the orthorhombic Sohncke type space group $P2_12_12$. The asymmetric unit of **2** consists of $[\text{CoL}^2_2]^+$ complex cation, half of molecule of the $[\text{Co}(\text{NCS})_4]^{2-}$ complex anion and one solvent water molecule. In the ORTEP presentation of **2** (**Fig. 2**) unlabelled complex cation and half of the complex anion are generated by the symmetry operation $-x, -y+1, z$. Solvent water molecules related by twofold axis of symmetry are not presented in **Fig. 2** for the sake of clarity. In the Co(III) complex **2** two deprotonated ligand molecules L^2 coordinate the central metal ion in a *mer* arrangement, forming an octahedral complex by chelation through two NNS sets of donor atoms. Each ligand molecule coordinates to metallic center through thiazole nitrogen, imine nitrogen and thiolate sulfur atoms. The chelate ligand donors–cobalt bond distances are: Co–N_{thiazole} [Co1–N1 1.958(5) Å, Co1–N5 1.962(6) Å, Co–N_{thiazole} (mean value) 1.960 Å], Co–N_{imine} [Co1–N2 1.903(5) Å, Co1–N6 1.911(5) Å, Co–N_{imine} (mean value) 1.907 Å] and Co–S_{thiolate} [Co1–S2 2.225(2) Å, Co1–S4 2.220(2) Å, Co–S_{thiolate} (mean value) 2.222 Å] (**Table 1** and **Table S2**). The Co–N_{thiazole}, Co–N_{imine} and Co–S_{thiolate} distances are in close agreement with those observed in related Co(III)-N₄S₂ complexes with thiosemicarbazone ligands [45–47], **Table S2** in the supplementary material. Although the Co(III) complex with the condensation product of 4-methyl-2-thiazolecarboxaldehyde and 4-phenylthiosemicarbazide [47] displays somewhat longer Co–N_{thiazole} distances. The tridentate coordination of each ligand molecule implies the formation of two fused five-membered chelate rings (Co–N–C–C–N and Co–N–N–C–S). Similarly, as in complex **1**, the chelate rings Co–N–C–C–N and Co–N–N–C–S are almost coplanar, as indicated by the dihedral angles of 1.5° for the rings fused along Co1–N2 and Co1–N6 bonds. The two chelation planes, comprising the atoms S–N–N–Co are also practically perpendicular, as indicated by the dihedral angle of 89.5°. Complex **2** displays somewhat smaller distortion from regular octahedral geometry compared to complex **1**, as indicated by the average ΔO_h value of 4.4°. In the crystals of complex **2** complex cations self-assemble within the layer parallel with the (0 1 0) lattice plain by means of intermolecular hydrogen bonds between terminal NH₂ group (N4) serving as hydrogen bond donor and thiolate sulfur atom S4 at $1/2+x, 3/2-y, 1-z$ and nitrogen atom N7 at $x, y, -1+z$ serving as acceptors (**Table**

3, Fig. 4). The $[\text{Co}(\text{NCS})_4]^{2-}$ anions in **1** and **2** have Co(II) centres with tetrahedral arrangements of NCS^- ligands. The NCS^- groups are almost linear but there is significant bending at the N10 atom in both **1** and **2**.

ORTEP-3 for Windows was used to prepare drawings [48].

3.5 Magnetic properties

The susceptibilities of **1** and **2** are shown in **Fig. 5**. They are almost the same, regardless the **1** have two cobalt ions per molecule (one Co^{3+} and one Co^{2+}), while **2** has two Co^{3+} ions and one Co^{2+} ion per molecule. The susceptibilities monotonically increase with decreasing temperature from 300 K down to 2 K. In the inset in Fig. 5 a temperature dependent effective magnetic moment is shown obtained as $\mu_{\text{eff}} = (8\chi T)^{1/2}$ [49]. The effective magnetic moments are practically constant between 20 K and 300 K: $4.2 \mu_{\text{B}}$ for **1**, and $4.1 \mu_{\text{B}}$ for **2**. No temperature dependence of the effective magnetic moment suggests there is no magnetic interaction between the magnetic moments. The values of the effective magnetic moments of $\sim 4 \mu_{\text{B}}$ are very close to the expected value of $3.9 \mu_{\text{B}}$ for Co^{2+} ion with spin $S = 3/2$ and completely quenched orbital angular momentum ($L = 0$) [50].

<Figure 5>

Considering both experimental results:

- (i) almost equal susceptibilities of **1** and **2** regardless of a different number of cobalt ions in a molecule, and
- (ii) the measured effective magnetic moment per molecule that is very close to the expected value for one Co^{2+} ion,

we can conclude the Co^{3+} ions in **1** and **2** are in a low spin magnetic state with $S = 0$ [51] and do not contribute to the magnetic signal.

A small decrease of the effective magnetic moment of **1** and **2** below 20 K can be attributed to the interaction between the crystalline electric field with the ionic charge distribution (zero field splitting). The parameter D was determined using a computer package PHI [52] and gave us (full green lines in inset in **Fig. 5**): $D = -1.5 \text{ cm}^{-1}$, $g = 2.18$ for **1**, and $D = -2.1 \text{ cm}^{-1}$, $g = 2.10$ for **2**.

4. Conclusion

Compounds **1** and **2** were obtained in reaction of $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and NH_4SCN with (*E*)-*N,N,N*-trimethyl-2-oxo-2-(2-(1-(pyridin-2-yl)ethylidene)hydrazinyl)ethan-1-aminium chloride (HL^+Cl) and (*E*)-2-(1-(thiazol-2-yl)ethylidene)hydrazine-1-carbothioamide (HL^2), respectively. Compounds **1** and **2** possess octahedral $\text{Co}(\text{III})$ complex cations which are formed by tridentate coordination of two deprotonated hydrazone ligands and the same complex anion $[\text{Co}(\text{NCS})_4]^{2-}$. NMR spectra of compounds **1** and **2** showed that their complex cations are stable in DMSO solution. Magnetic susceptibilities of **1** and **2** are almost the same and slowly increase at lower temperatures. Measured effective magnetic moments ($4.2 \mu_{\text{B}}$ for **1**, and $4.1 \mu_{\text{B}}$ for **2**) are practically constant between 20 K and 300 K and very close to the expected value ($3.9 \mu_{\text{B}}$) for Co^{2+} ion with spin $S = 3/2$ and completely quenched orbital angular momentum ($L = 0$). Co^{3+} ions in octahedral cations of compounds **1** and **2** are in a low spin magnetic state with $S = 0$ and do not contribute to the magnetic moment.

Appendix A. Supplementary data

CCDC 1854179 (for **1**) and 1854180 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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Table 1. Crystal data, structure refinement details, selected bond lengths (Å) and angles (°) for complexes **1** and **2**.

	1	2
formula	C ₂₈ H ₃₆ BCo ₂ F ₄ N ₁₂ O ₂ S ₄	C ₂₈ H ₃₂ Co ₃ N ₂₀ O ₂ S ₁₂
Fw (g mol ⁻¹)	905.60	1242.24
crystal size (mm)	0.60 × 0.30 × 0.05	0.20 × 0.20 × 0.05
crystal color	green	green
crystal system	monoclinic	orthorhombic
space group	<i>P2₁/c</i>	<i>P2₁2₁2</i>
<i>a</i> (Å)	14.8835(9)	11.9146(6)
<i>b</i> (Å)	11.0183(6)	24.332(2)
<i>c</i> (Å)	25.1482(19)	8.7445(5)
β (°)	97.677(6)	90
<i>V</i> (Å ³)	4087.1(5)	2535.1(3)
<i>Z</i>	4	2
calcd density (g cm ⁻³)	1.472	1.627
<i>F</i> (000)	1852	1258
no. of collected reflns	28240	12681
no. of independent reflns	9369	5520
<i>R</i> _{int}	0.0485	0.0481
no. of reflns observed	4744	3904
no. parameters	486	300
<i>R</i> [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0707	0.0553
<i>wR</i> ₂ (all data) ^b	0.2409	0.1288
<i>Goof</i> , <i>S</i> ^c	1.049	1.025
maximum/minimum residual electron density (e Å ⁻³)	+0.94/-0.86	+0.56/-0.40

1		2	
Co1-O1	1.903(3)	Co1-S2	2.225(2)
Co1-O2	1.909(3)	Co1-S4	2.220(2)
Co1-N1	1.917(4)	Co1-N1	1.958(5)
Co1-N2	1.853(3)	Co1-N2	1.903(5)
Co1-N5	1.926(4)	Co1-N5	1.962(6)
Co1-N6	1.853(4)	Co1-N6	1.911(5)
O1-C8	1.302(5)	N2-N3	1.352(7)
O2-C20	1.301(6)	N6-N7	1.363(8)
N2-N3	1.391(5)	N2-C4	1.320(7)
N2-C6	1.282(5)	N6-C10	1.290(9)
N3-C8	1.289(5)	N3-C6	1.319(8)
N6-N7	1.396(5)	N7-C12	1.315(9)
N6-C18	1.291(6)	Co2-N9	1.957(10)
N7-C20	1.315(7)	Co2-N10	1.963(8)
Co2-N9	1.954(6)	S5-C13	1.583(12)
Co2-N10	1.961(7)	S6-C14	1.598(10)
Co2-N11	1.933(6)	N9-C13	1.148(12)
Co2-N12	1.955(6)	N10-C14	1.164(11)
S1-C25	1.616(8)	S2-C6	1.739(6)
S2-C26	1.596(8)	S4-C12	1.736(7)
S3-C27	1.604(8)		
S4-C28	1.607(7)		
N9-C25	1.146(8)		
N10-C26	1.148(8)		
O1-Co1-O2	91.2(2)	S4-Co1-S2	91.61(8)
O1-Co1-N1	165.19(14)	N1-Co1-S2	167.7(2)
O1-Co1-N5	89.38(14)	N1-Co1-S4	91.2(2)
O2-Co1-N1	88.6(2)	N1-Co1-N5	90.2(2)
O2-Co1-N5	165.4(2)	N2-Co1-S2	85.4(2)
N1-Co1-N5	94.6(2)	N2-Co1-S4	91.8(2)
N2-Co1-O1	82.63(14)	N2-Co1-N1	82.5(2)
N2-Co1-O2	94.7(2)	N2-Co1-N5	100.5(3)
N2-Co1-N1	82.6(2)	N2-Co1-N6	176.4(2)
N2-Co1-N5	99.9(2)	N5-Co1-S2	89.6(2)
N2-Co1-N6	175.8(2)	N5-Co1-S4	167.7(2)
N6-Co1-O1	94.2(2)	N6-Co1-S2	97.2(2)
N6-Co1-O2	82.7(2)	N6-Co1-S4	85.6(2)
N6-Co1-N1	100.5(2)	N6-Co1-N1	95.0(2)
N6-Co1-N5	82.7(2)	N6-Co1-N5	82.0(3)
N9-Co2-N10	113.4(3)	N9-Co2-N9 ⁱ	111.3(6)
N9-Co2-N12	109.7(2)	N9-Co2-N10 ⁱ	104.4(4)
N11-Co2-N9	109.7(3)	N9-Co2-N10	106.8(4)
N11-Co2-N10	109.1(3)	N10-Co2-N10 ⁱ	123.1(6)
N11-Co2-N12	108.0(3)	N9-C13-S5	178.8(10)
N12-Co2-N10	106.8(2)	N10-C14-S6	178.3(10)
N9-C25-S1	177.9(7)	Co2-N9-C13	177.4(9)
N10-C26-S2	177.6(8)	Co2-N10-C14	156.8(10)
N11-C27-S3	176.3(8)		

N12-C28-S4	178.0(5)
Co2-N9-C25	171.3(6)
Co2-N10-C26	157.9(6)
Co2-N11-C27	174.4(7)
Co2-N12-C28	177.8(5)

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

^c $S = \{ \sum [(F_o^2 - F_c^2)^2] / (n/p) \}^{1/2}$ where n is the number of reflections and p is the total number of parameters refined. Symmetry code: (i) $-x, -y+1, z$.

Table 2. Hydrogen-bond parameters for complex 1.

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	Symm. operation on A
C9-H9B...F1	0.97	2.41	3.310(6)	154	
C19-H19A...F4	0.96	2.35	3.278(7)	162	$x, -1+y, z$
C22-H22A...F1	0.96	2.51	3.088(9)	119	
C22-H22B...F3	0.96	2.40	3.031(14)	123	

Table 3. Hydrogen-bond parameters for complex 2.

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)	Symm. operation on A
N4-H4A...N7	0.86	2.28	3.065(8)	152	$x, y, -1+z$
N4-H4B...S4	0.86	2.74	3.555(6)	159	$1/2+x, 3/2-y, 1-z$

Figure caption

Figure 1. The ORTEP drawing of $[\text{CoL}^1_2]^{3+}$ complex cation in **1**. Thermal ellipsoids are drawn at the 30% probability level.

Figure 2. The ORTEP drawing of complex **2**. Thermal ellipsoids are drawn at the 30% probability level.

Figure 3. Perspective view of crystal packing of **1** showing hydrogen-bonded chains generated by means of C–H...F hydrogen bonds between complex cations and BF_4^- anions. Thermal ellipsoids are drawn at the 30% probability level.

Figure 4. Crystal packing of **2** viewed normal to (010) showing self-assembled complex cations within a layer parallel with the (010) lattice plane by means of N–H...N and N–H...S hydrogen bonds. Thermal ellipsoids are drawn at the 30% probability level.

Figure 5. Temperature dependent susceptibility and effective magnetic moment (inset) of **1** and **2**. The full green lines are fits using a program PHI and taking into account crystal field effect.

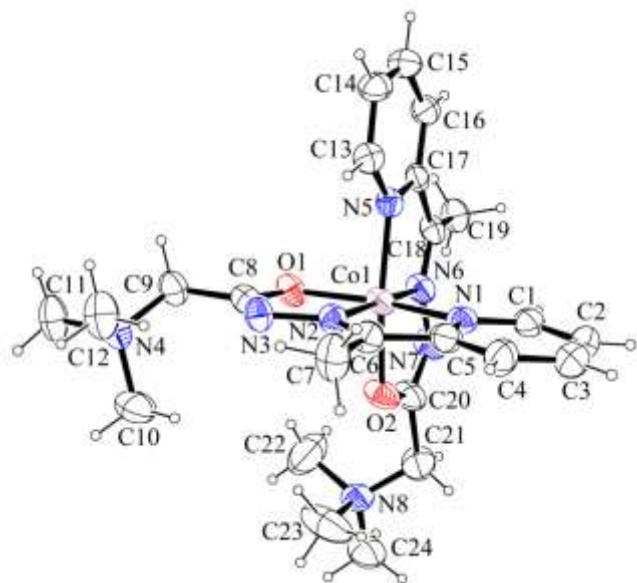


Figure 1. The ORTEP drawing of $[\text{CoL}_2]^{3+}$ complex cation in **1**. Thermal ellipsoids are drawn at the 30% probability level.

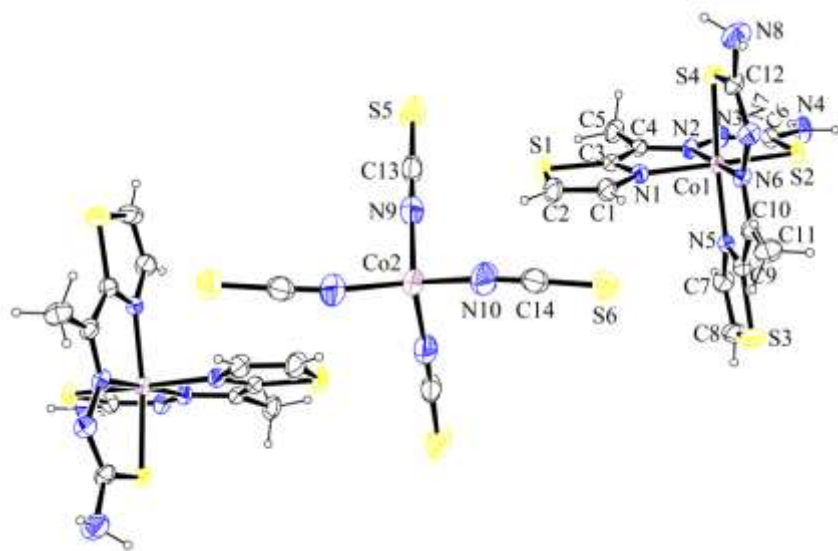


Figure 2. The ORTEP drawing of complex **2**. Thermal ellipsoids are drawn at the 30% probability level.

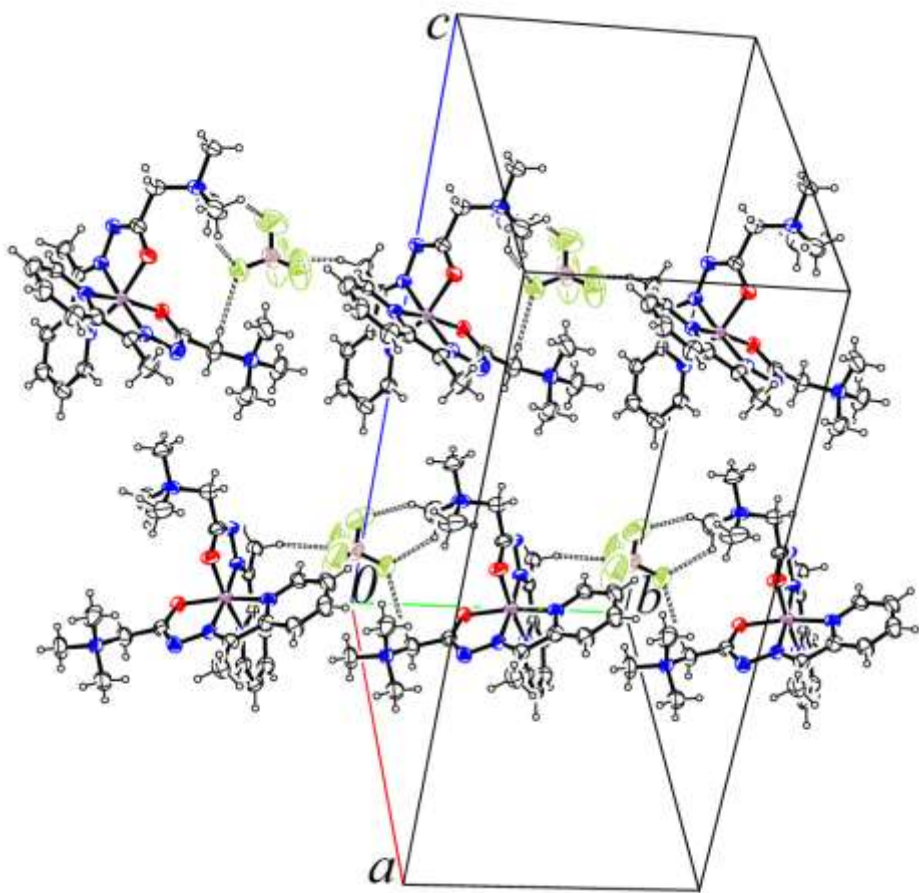


Figure 3. Perspective view of crystal packing of **1** showing hydrogen-bonded chains generated by means of C–H...F hydrogen bonds between complex cations and BF₄⁻ anions. Thermal ellipsoids are drawn at the 30% probability level.

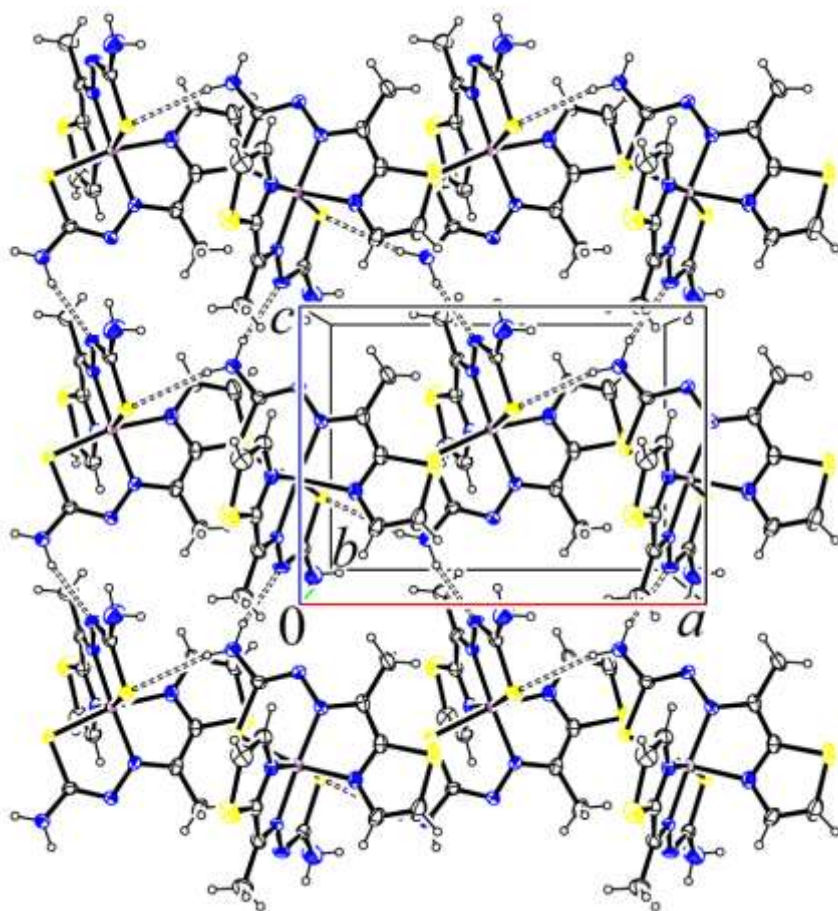


Figure 4. Crystal packing of **2** viewed normal to (010) showing self-assembled complex cations within a layer parallel with the (010) lattice plane by means of N-H...N and N-H...S hydrogen bonds. Thermal ellipsoids are drawn at the 30% probability level.

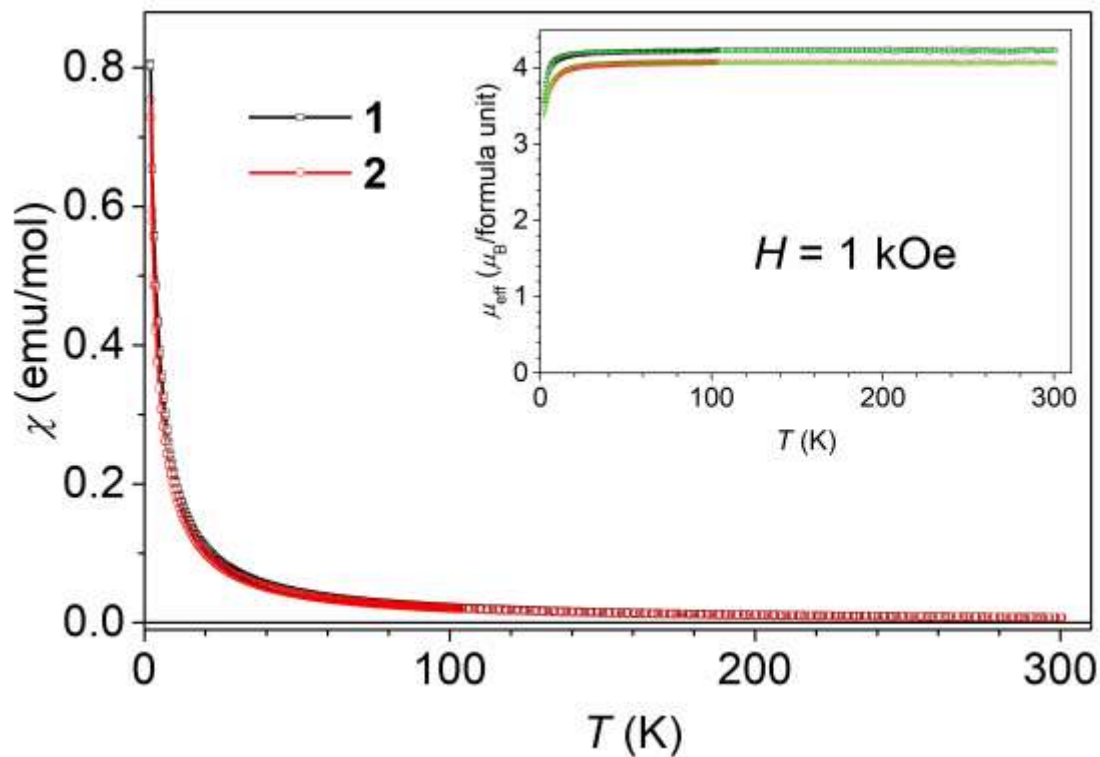
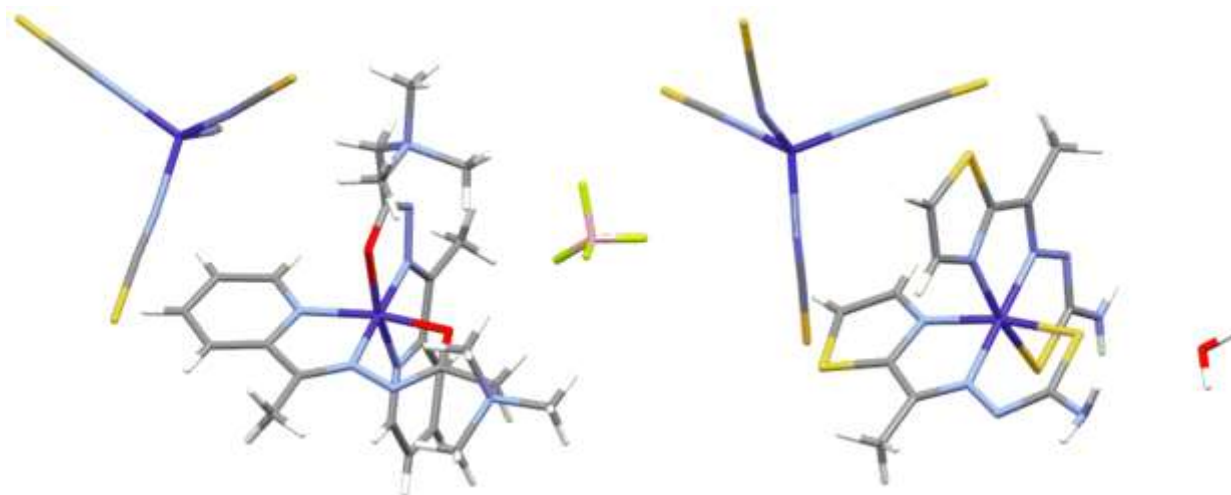


Figure 5. Temperature dependent susceptibility and effective magnetic moment (inset) of **1** and **2**. The full green lines are fits using a program PHI and taking into account crystal field effect.



Crystal structures and magnetic properties of octahedral Co(III) complexes with heteroaromatic hydrazones and tetraisothiocyanato Co(II) anions.