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Crystal structures of bis[1-(1-hydroxypropan-2-ylidene)thiosemicarbazide- κ^3S,N,O]cobalt(III)-tetra(thiocyanato- κN) cobalt(II) methanol solvate, bis{1-(1-hydroxypropan-2-ylidene)thiosemicarbazide- κ^3S,N,O }nickel(II) bis(thiocyanate) and (1-(1-hydroxypropan-2-ylidene)thiosemicarbazide- κ^3S,N,O)bis(thiocyanato- κN)zinc(II)

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ABSTRACT



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The reactions of Schiff base 1-(1-hydroxypropan-2-ylidene)thiosemicarbazide (H_2L), with salt of thiocyanate metal (II) (Co, Ni, or Zn), provided one dinuclear and two new mononuclear complexes, formulated respectively as $\{[Co(LH)_2]_2 \cdot [Co(NCS)_4] \cdot 2(MeOH)\}$ (1), $\{[Ni(H_2L)_2] \cdot [Ni(NCS)_2]\}$ (2) and $[Zn(H_2L)(NCS)_2]$ (3). These compounds have been studied and characterized by elemental analysis, infrared, and ultraviolet-visible (UV-vis) spectroscopies. The structures of the three complexes have been resolved by X-ray crystallography technique. The dinuclear complex 1 crystallizes in the orthorhombic space group $Fdd2$ with the following unit cell parameters $a = 33.1524$ (3) Å, $b = 19.3780$ (2) Å, $c = 13.2533$ (2) Å, $V = 8514.28$ (17) Å³, $Z = 16$, $R_1 = 0.025$ and $wR_2 = 0.063$, the mononuclear complex 2 crystallizes in the monoclinic space group $P2_1/n$ with the following unit cell parameters $a = 11.5752$ (1) Å, $b = 12.3253$ (1) Å, $c = 14.2257$ (2) Å, $\beta = 106.855$ (1)°, $V = 1942$ (4) Å³, $Z = 4$, $R_1 = 0.038$ and $wR_2 = 0.106$ and the mononuclear complex 3 crystallizes in the monoclinic space group $P2_1/c$ with the following unit cell parameters $a = 6.1121$ (2) Å, $b = 26.8272$ (7) Å, $c = 8.0292$ (2) Å, $\beta = 99.876$ (3)°, $V = 1297.04$ (6) Å³, $Z = 4$, $R_1 = 0.026$ and $wR_2 = 0.057$. The asymmetric unit of Complex 1 contains one cationic unit in which the ligand acts in its monodeprotonated form in tridentate fashion and one half of the anionic unit containing two thiocyanate co-ligands. In complexes 2 and 3, the ligand acts in its neutral form in a tridentate manner. In complex 2, two ligand molecules coordinate the Ni(II) center, and the thiocyanate moieties remains uncoordinated. In complex 3, the Zn(II) is coordinated by one ligand molecule and two thiocyanate groups through their nitrogen atoms. Numerous hydrogen bonds consolidated the structures of complexes 1, 2, and 3 in a three-dimensional network.

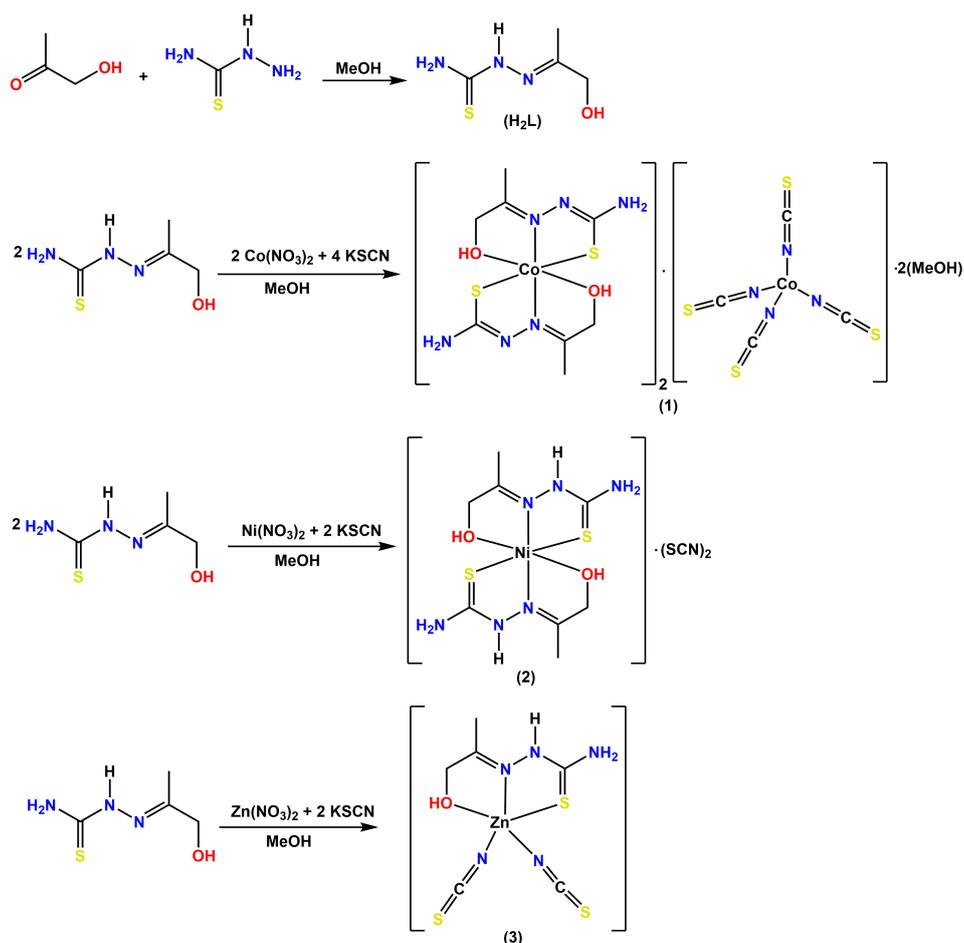
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1. Introduction

The Schiff bases formed from the condensation reaction between thiosemicarbazide and a carbonyl compound are widely studied in organic chemistry and coordination chemistry. In fact, thiosemicarbazide and its derivatives have interesting biological properties [1-3]. Organic molecules obtained from thiosemicarbazide which have shown antioxidant [4,5], antitumor [5,6], antituberculosis [7,8], antifungal [7,9], antibacterial [7,10] or analgesic [11] properties are largely reported in the literature. To improve the properties of these derivatives, many metals transition [12-14] and tin complexes [15-17] were prepared from these types of Schiff bases. In addition to the important biological properties observed, physical properties [18,19] are discovered owing to

the presence of a metallic center in the molecular structures formed. The original structures of these compounds induce physical properties such as magnetism [20-22], fluorescence [23-25] or catalytic [26-28] in lanthanides and transition metals complexes. Detailed studies of the molecular structures and mode of coordination of these Schiff bases are carried out. The thiosemicarbazide moiety can complex in various ways. Indeed, a thione/thiol equilibrium can be established. Thus, the sulfur atom can bind to the metal in its thione form or in its thiolate form [29-31]. There are also complexes in which the sulfur atom remains uncoordinated [32,33]. In this article, we report the synthesis and structural characterization of the Co(II/III), Ni(II) and Zn(II) complexes of 1-(1-hydroxypropan-2-ylidene)thiosemicarbazide (H_2L) (Scheme 1).



Scheme 1. Synthetic scheme for the preparation of H₂L and complexes.

2. Experimental

2.1. Materials and instrumentation

Thiosemicarbazide, 1-hydroxyacetone, potassium thiocyanate, cobalt nitrate hexahydrate, nickel nitrate hexahydrate and zinc nitrate hexahydrate were purchased from Sigma-Aldrich and used as received without further purification. All solvents used were of reagent grade. Melting points were determined on a Büchi 570 melting-point apparatus and were uncorrected. Elemental analyses of C, H, and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on an FTIR Spectrum Two of the Perkin Elmer spectrometer in the 4000-400 cm⁻¹ region. UV-vis spectra were recorded using a PerkinElmer Lambda UV-vis spectrophotometer. The ¹H and ¹³C NMR spectra of the Schiff bases were recorded in DMSO-*d*₆ on a BRUKER 500 MHz spectrometer at room temperature using TMS as internal reference.

2.2. Synthesis of ligand 1-(1-hydroxypropan-2-ylidene)thiosemicarbazide (H₂L)

The compound H₂L is synthesized using the method reported by Netalkar *et al.* [34] with a slight modification. In a 250 mL flask containing 30 mL of methanol, 16.460 mmol (1.5 g) was introduced. A methanol solution containing 16.460 mmol (1.130 mL) of 1-hydroxyacetone was added and the mixture was refluxed for 4 hours. On cooling, the beige solution gives a white precipitate, which is recovered by filtration,

washed with 2×20 mL of methanol, then 20 mL of diethyl ether, and dried in a desiccator.

1-(1-Hydroxypropan-2-ylidene)thiosemicarbazide (H₂L): Color: White. Yield: 80 %. M.p.: 175-176 °C. FT-IR (KBr, ν, cm⁻¹): 3428 (OH), 3379 (NH₂), 3218, 3164 (N-H), 1660 (C=N), 1259 (C=S), 1068 (C-O). ¹H NMR (500 MHz, DMSO-*d*₆, δ, ppm): 10.01 (s, 1H, NH), 7.90, 8.06 (s, 2H, NH₂), 4.88 (s, 1H, OH), 4.01 (s, 2H, -CH₂-OH), 1.87 (s, 3H, -CH₃). ¹³C NMR (125 MHz, DMSO-*d*₆, δ, ppm): 14.15 (-CH₃), 65.36 (-CH₂-OH), 153.08 (C=N), 179.54 (C=S). Anal. calc. for C₄H₉N₃OS: C, 32.64; H, 6.16; N, 28.55. Found: C, 32.61; H, 6.14; N, 28.51%. UV-Vis (λ_{max}, nm): 277

2.3. Synthesis of complexes 1, 2, and 3

In a 50 mL round bottomed flask, 0.6793 mmol of H₂L, were dissolved in 10 mL of methanol. 20 mL of methanol containing 0.6793 mmol of cobalt nitrate hexahydrate and 2.7172 mmol of potassium thiocyanate was filtered and added to the above solution (for the nickel complex 0.6793 mmol of the ligand H₂L, 0.3396 mmol of nickel nitrate hexahydrate and 0.6793 mmol of potassium thiocyanate were used; for the zinc complex 0.6793 mmol of H₂L, 0.6793 mmol of zinc nitrate hexahydrate and 1.3586 mmol of potassium thiocyanate were used). The resulting solution was refluxed for 2 hours before being filtered. The filtrates were left to slow evaporation. After a week, orange crystals for cobalt (**1**), green for nickel (**2**) and colorless for zinc complex (**3**) were recovered.

Bis[1-(1-hydroxypropan-2-ylidene)thiosemicarbazide-κ³S, N, O]cobalt(III)-tetra(thiocyanato-κN)cobalt(II) methanol solvate (**1**): Color: Orange. Yield: 55 %. FT-IR (KBr, ν, cm⁻¹): 3438, 3371

Table 1. Crystal data and structure refinement for compounds **1**, **2**, and **3**.

Compound	1	2	3
Empirical formula	C ₂₂ H ₄₀ C ₀₃ N ₁₆ O ₆ S ₈	C ₁₀ H ₁₈ N ₈ NiO ₂ S ₄	C ₆ H ₉ N ₅ OS ₃ Zn
Formula weight	1057.98	469.27	328.73
Temperature (K)	295(2)	295(2)	295(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Fdd2</i>	<i>P2₁/n</i>	<i>P2₁/c</i>
<i>a</i> , (Å)	33.1524(3)	11.57520(10)	6.1121(2)
<i>b</i> , (Å)	19.3780(2)	12.32530(10)	26.8272(7)
<i>c</i> , (Å)	13.2533(2)	14.2257(2)	8.0292(2)
α (°)	90	90	90
β (°)	90	106.8550(10)	99.876(3)
γ (°)	90	90	90
Volume (Å ³)	8514.28(17)	1942.36(4)	1297.04(6)
<i>Z</i>	8	4	4
ρ_{calc} (g/cm ³)	1.651	1.605	1.683
μ (mm ⁻¹)	1.604	5.672	2.363
<i>F</i> (000)	4328.0	968.0	664.0
Crystal size (mm ³)	0.32 × 0.18 × 0.06	0.36 × 0.2 × 0.2	0.1 × 0.1 × 0.1
Radiation	MoK α (λ = 0.71073)	CuK α (λ = 1.54184)	MoK α (λ = 0.71073)
2 θ range for data collection (°)	3.92 to 58.232	8.708 to 145.628	5.37 to 59.162
Index ranges	-45 ≤ <i>h</i> ≤ 45 -25 ≤ <i>k</i> ≤ 25 -18 ≤ <i>l</i> ≤ 17	-12 ≤ <i>h</i> ≤ 14 -14 ≤ <i>k</i> ≤ 15 -17 ≤ <i>l</i> ≤ 17	-7 ≤ <i>h</i> ≤ 8 -36 ≤ <i>k</i> ≤ 36 -11 ≤ <i>l</i> ≤ 10
Reflections collected	73314	16439	28641
Independent reflections	5395 [R _{int} = 0.0338, R _{sigma} = 0.0136]	3814 [R _{int} = 0.0348, R _{sigma} = 0.0269]	3372 [R _{int} = 0.0250, R _{sigma} = 0.0142]
Data/restraints/parameters	5395/1/253	3814/6/234	3372/0/181
Goodness-of-fit on <i>F</i> ²	1.048	1.027	1.097
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0253, wR ₂ = 0.0615	R ₁ = 0.0378, wR ₂ = 0.1023	R ₁ = 0.0258, wR ₂ = 0.0546
Final R indexes [all data]	R ₁ = 0.0278, wR ₂ = 0.0633	R ₁ = 0.0402, wR ₂ = 0.1061	R ₁ = 0.0321, wR ₂ = 0.0571
Largest diff. peak/hole (e.Å ⁻³)	0.58/-0.33	0.54/-0.45	0.33/-0.31

Table 2. Selected bond lengths for complexes **1**, **2**, and **3**.

Complex 1			Complex 2			Complex 3		
Atom	Atom	Length (Å)	Atom	Atom	Length (Å)	Atom	Atom	Length (Å)
Co1	N1	1.887(2)	Ni1	N4	2.0018(15)	Zn1	S1	2.4335(5)
Co1	N4	1.892(2)	Ni1	N1	2.0057(15)	Zn1	O1	2.1846(16)
Co1	O2	1.989(2)	Ni1	O2	2.1234(14)	Zn1	N1	2.0973(15)
Co1	O1	2.013(2)	Ni1	O1	2.1240(14)	Zn1	N4	1.9576(16)
Co1	S1	2.1818(8)	Ni1	S2	2.3867(5)	Zn1	N5	1.9743(18)
Co1	S2	2.1843(8)	Ni1	S1	2.3983(5)	S1	C4	1.6959(18)
Co2	N8	1.942(4)	S1	C4	1.698(2)	S3	C6	1.634(2)
Co2	N7 ⁱ	1.955(4)	S2	C8	1.695(2)	S2	C5	1.622(2)
S2	C4	1.735(3)	N2	C4	1.344(3)	N4	C5	1.144(2)
S3	C10	1.610(4)	N5	C8	1.344(3)	N5	C6	1.148(2)

Symmetry code: (i) -x+1, -y, z.

(OH), 3331 (NH₂), 2065, 2014 (SCN), 1640 (C=N), 1224 (C=S), 1049 (C-O). Anal. calc. for C₂₂H₄₀C₀₃N₁₆O₆S₈: C, 24.98; H, 3.81; N, 21.18. Found: C, 24.95; H, 3.79; N, 21.13%. UV-Vis (λ_{max} , nm): 267, 280, 530.

Bis{1-(1-hydroxypropan-2-ylidene)thiosemicarbazide- κ^3 S, N, O}nickel(II)*bis*(thiocyanate) (**2**): Color: Green. Yield: 62 %. FT-IR (KBr, ν , cm⁻¹): 3378 (OH), 3252 (NH₂), 3159 (N-H), 2039 (SCN), 1660 (C=N), 1259 (C=S), 1049 (C-O). Anal. calc. for C₁₀H₁₈N₈O₂S₄Ni: C, 25.60; H, 3.87; N, 23.88. Found: C, 25.56; H, 3.86; N, 23.85%. UV-Vis (λ_{max} , nm): 277, 483, 816.

(1-(1-Hydroxypropan-2-ylidene)thiosemicarbazide- κ^3 S, N, O)bis(thiocyanato- κ N)zinc(II) (**3**): Color: Colorless. Yield: 74 %. FT-IR (KBr, ν , cm⁻¹): 3357 (OH), 3265 (NH₂), 3170, (N-H), 2100 (SCN), 1660 (C=N), 1259 (C=S), 1052 (C-O). Anal. calc. for C₆H₉N₅OS₃Zn: C, 21.92; H, 2.76; N, 21.30. Found: C, 21.90; H, 2.74; N, 21.21%. UV-Vis (λ_{max} , nm): 280.

2.4. X-ray data collection, structure determination, and refinement

Single crystals of **1**, **2** and **3** were grown by slow evaporation of methanol solution of the corresponding complex. Suitable crystals were selected and mounted on a Rigaku Oxford Diffraction SuperNova diffractometer at the MoK α radiation for compounds **1** and **3** and at the CuK α radiation for compound **2**. The crystals were kept at 295(2) K during data collection. Details of the X-ray crystal structure solution and refinement are given in Table 1. Using Olex2 [35], the structure was solved with the SHELXT [36] structure solution program

using direct methods and refined with the SHELXL [37] refinement package. The crystallographic details of compounds **1**, **2** and **3** are summarized in Table 1, and the bond lengths, bond angles of compounds **1**, **2** and **3** are listed in Tables 2 and 3, respectively.

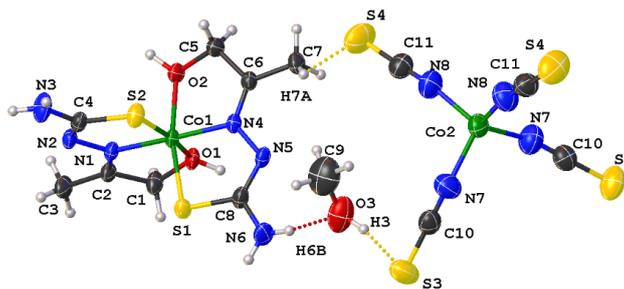
3. Results and discussion

3.1. General study

The H₂L ligand is synthesized according to the procedure of Scheme 1. It is obtained in the form of a pure white powder with a yield of 80% and a melting point of 175-176 °C. The compound was characterized by spectroscopic methods such as FTIR and ¹H and ¹³C NMR. The FTIR spectrum gives several characteristic bands. The broad band at 3428 cm⁻¹ indicates the presence of a hydroxy group in the molecule. The bands at 3379 and 3218 cm⁻¹ are attributed to antisymmetric vibration and symmetric vibration of the -NH₂ amino group [38]. The band at 3164 cm⁻¹ is due to the elongation of the N-H bond of the hydrazinyl group [39]. The band due to the C=N moiety is pointed at 1660 cm⁻¹ while the characteristic bands due to the thioamide NH-C=S moieties are pointed at 1259 and 795 cm⁻¹. The absence of the band characteristic of the S-H, expected at ca. 2600 cm⁻¹, indicates that the compound is only in its thione form. The ¹H NMR spectrum of the ligand shows a broad signal characteristic of the OH group at δ 4.88 ppm. The signals at δ 7.90 and 8.06 ppm are, respectively, attributed to the two protons of the -NH₂ group. The signal at δ 10.01 ppm is due to the -NH proton.

Table 3. Selected bond angles for complexes **1**, **2**, and **3**.

Complex 1				Complex 2				Complex 3			
Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)	Atom	Atom	Atom	Angle (°)
N1	Co1	N4	176.71(9)	N4	Ni1	N1	169.08(6)	O1	Zn1	S1	150.09(5)
N1	Co1	O2	95.41(9)	N4	Ni1	O1	93.25(6)	N4	Zn1	S1	100.55(5)
N4	Co1	O1	96.30(9)	N1	Ni1	O1	77.71(6)	N4	C5	S2	179.14(18)
O2	Co1	S1	168.55(6)	O2	Ni1	S2	161.09(4)	C5	N4	Zn1	169.45(18)
S1	Co1	S2	90.80(3)	O1	Ni1	S2	95.78(4)	N4	Zn1	N1	135.67(7)
N8	Co2	N8 ⁱ	110.5(3)	N4	Ni1	S1	104.76(5)	N5	Zn1	S1	104.52(6)
N8 ⁱ	Co2	N7 ⁱ	107.24(17)	O1	Ni1	S1	160.09(4)	N4	Zn1	N5	114.48(8)
N8	Co2	N7	107.24(17)	S2	Ni1	S1	94.74(2)	N5	Zn1	N1	107.54(7)
N7	C10	S3	179.2(4)	N7	C9	S3	179.6(2)	N5	C6	S3	178.31(19)
N8	C11	S4	178.1(4)	N8	C10	S4	176.1(2)	C6	N5	Zn1	168.74(18)

Symmetry code: (i) $-x+1, -y, z$.**Figure 1.** Single crystal structure of complex **1**.

Two singlet signals at δ 4.01 and 1.87 ppm are also observed, attributed to the $-\text{CH}_2-$ and $-\text{CH}_3$ groups, respectively. Two characteristic signals from the azomethine ($\text{C}=\text{N}$) and thiocarbonyl ($\text{C}=\text{S}$) carbon atoms are pointed at δ 153.08 and 179.54 ppm, respectively in the ^{13}C NMR spectrum.

The complexes were synthesized using a 1:2:1 molar ratio of $\text{M}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, ($\text{M} = \text{Co}, \text{Ni}, \text{or Zn}$), KNCS and H_2L in MeOH solution under reflux. Upon coordination of the ligand to the metal ions, the infrared spectra of the resulting complexes **2** and **3** still show bands attributed to the $-\text{NH}_2$, $-\text{NH}-$ and $-\text{OH}$ groups with small shifts. This observation shows that the ligand acts in its neutral form in these two complexes. However, for complex **1**, the band due to hydrazinyl $-\text{NH}$ disappeared from the spectrum. The ligand acts in its mono deprotonated form. In addition, a band pointed at 3438 cm^{-1} is indicative of the presence of an $-\text{OH}$ group. For all three complexes, the bands due to the azomethine group undergo a strong displacement. The complex **2** shows a $\text{C}=\text{N}$ band at 1610 cm^{-1} and a $\text{C}=\text{S}$ bands at 1225 cm^{-1} and 759 cm^{-1} , while complex **3** exhibits bands at 1604 cm^{-1} for $\text{C}=\text{N}$ and bands at 1248 cm^{-1} and 755 cm^{-1} for $\text{C}=\text{S}$. For complex **1**, the $\text{C}=\text{N}$ band is pointed at 1640 cm^{-1} and the bands characteristic of $\text{C}=\text{S}$ are pointed at 1224 and 741 cm^{-1} .

The shifts of these bands compared to the bands of the free ligand indicate that the nitrogen atom of the azomethine and the sulfur atom of the thiocarbonyl are involved in the coordination of the metal in complexes **1**, **2**, and **3**. The sharp intense band observed in the ligand spectrum at 1068 cm^{-1} and attributed to the $\text{C}-\text{O}$ single bond in the free ligand undergoes a $16-19\text{ cm}^{-1}$ shift to lower frequencies in the spectra of the complexes. This fact is indicative of the involvement of the oxygen atom of the alcohol function in the coordination. Thus, it is observed that in all the complexes the ligand acts as a tridentate ligand through the sulfur atom of the thioamide function, the nitrogen atom of the azomethine function and the oxygen atom of the alcoholic function. The amino and hydrazinyl nitrogen atoms remain uncoordinated. For all the complexes, the presence of thiocyanate groups is observed. The infrared spectrum of complex **1** gives two bands pointed at 2065 and 2014 cm^{-1} . The duplication of these bands suggests the presence of two non-equivalent thiocyanate groups [40]. The IR spectra of complexes **2** and **3** show a band attributed to the thiocyanate group at 2100 and 2039 cm^{-1} , respectively. The

position of the bands shows non-coordination or coordination of the thiocyanate group through the nitrogen atom [41-43]. In the electronic spectrum of the ligand, an intense band at 277 nm is attributed to the intraligand $n \rightarrow \pi^*$ transition associated with the $\text{C}=\text{N}$ and $\text{C}=\text{S}$ groups. This band is observed in all complexes with a variation of λ_{max} from 0 to 3 nm . The UV-visible spectrum of complex **1** shows another band at 267 nm , which is due to a $\pi \rightarrow \pi^*$ transition in the $\text{S}=\text{C}=\text{N}^-$ thiocyanate moiety. The crystal field theory of low spin octahedral $\text{Co}(\text{III})$ complex predicted two spin allowed $d-d$ transitions, namely $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$. The electronic spectrum of complex **1** showed a band as a shoulder at 530 nm assigned to one of the two expected transitions [44]. $\text{Ni}(\text{II})$ complex **2** gives two other bands at 480 nm and 816 nm . In the case of $\text{Ni}(\text{II})$ complex, three transitions $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}(\text{F})$ (ν_1), $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})$ (ν_2), and $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{P})$ (ν_3) are predicted [45]. The band at 483 nm can be attributed to the transition $^3\text{A}_{2g} \rightarrow ^3\text{T}_{1g}(\text{F})$ (ν_2) while the band at 816 nm is attributed to the transition $^3\text{A}_{2g} \rightarrow ^3\text{T}_{2g}(\text{F})$ (ν_1) [46,47].

3.2. Description of the structures

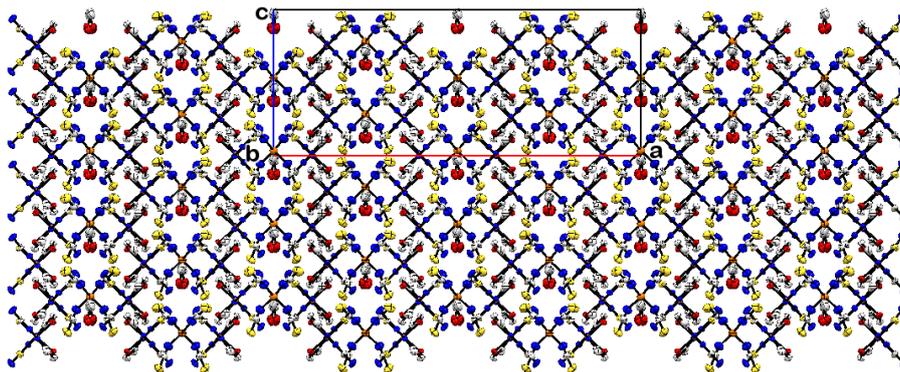
3.2.1. Complex 1

The compound **1** crystallizes in the orthorhombic system with the space group $Fdd2$. The selected bond distances and angles relevant to the coordination sphere of the complex are given in Tables 2 and 3, respectively. The ORTEP representation of the complex **1** formulated as $\{[\text{Co}(\text{LH})_2]_2 \cdot [\text{Co}(\text{NCS})_4] \cdot 2(\text{MeOH})\}$ is shown in Figure 1. The cobalt(II) center of the anionic unit formed by the tetrathiocyanatocobalt moiety is located on the crystallographic two fold axis of the $Fdd2$ space group and accounts for only $1/2$ in the asymmetric unit. Thus, the asymmetric unit contains 0.5 tetrathiocyanatocobalt moiety, one $\text{Co}(\text{III})$ ion, two mononegative ligands (HL^-), and one uncoordinated methanol molecule. The $\text{Co}(\text{III})$ ion is coordinated by two mono-deprotonated ligand which act in tridentate fashion, yielding a hexacoordinated metal ion. Each ligand molecule is coordinated to the $\text{Co}(\text{III})$ cation through one alcoholic oxygen atom, one azomethine nitrogen atom, and one sulfur atom. The $\text{N}_2\text{O}_2\text{S}_2$ environment around $\text{Co}(\text{III})$ is best described as a distorted octahedral geometry, the basal plane being occupied by $\text{O}1$, $\text{N}1$, $\text{S}2$, and $\text{N}4$.

Table 4. Hydrogen-bond geometry (Å, °) for complex 1.

D	H	A	D-H	H...A	D-A	∠D-H...A
O1	H1	N2 ⁱ	0.85	1.81	2.643(3)	165.9
N6	H6B	O3	0.86	2.07	2.915(5)	166.7
N3	H3A	S3 ⁱⁱⁱ	0.92	2.81	3.646(3)	152.4
N3	H3B	O1 ⁱⁱⁱ	0.85	2.61	3.109(4)	118.7
C3	H3E	S1 ⁱⁱⁱ	0.96	2.86	3.740(4)	153.7
O3	H3	S3	0.89	2.51	3.348(3)	158.6
O3	H3	N3 ^{iv}	0.89	2.70	3.122(4)	110.8
C7	H7A	S4	0.96	3.02	3.769(3)	136.2
C7	H7C	S2 ⁱ	0.96	2.88	3.801(4)	160.4
O2	H2	N5 ⁱⁱⁱ	0.92	1.82	2.715(3)	162.0
C5	H5B	O3 ⁱⁱⁱ	0.97	2.54	3.253(4)	130.6
C9	H9A	N2 ^v	0.96	2.55	3.474(6)	161.8

Symmetry codes: (i) $-x+5/4, y-1/4, z-1/4$; (ii) $x, y+1/2, z+1/2$; (iii) $-x+5/4, y+1/4, z+1/4$; (iv) $x, y-1/2, z-1/2$; (v) $-x+1, -y+1, z$.

**Figure 2.** Packing diagram of complex 1 viewed along the *b*-axis.

The *transoid* angle values are $S2-Co1-O1 = 168.55(6)^\circ$ and $N1-Co1-N4 = 176.71(9)^\circ$ while the *cisoid* angle is in the range $81.33(9)-96.30(9)^\circ$. These values deviate from the ideal values of 180° and 90° confirming the distortion of the octahedron. Furthermore, the angle defined by the S1 and O2 atoms occupying the apical positions, which is $168.55(6)^\circ$, deviates severely from the ideal value of 180° . The two ligand molecules are quite planar (RMS 0.1072 \AA and 0.0689 \AA) and form a dihedral angle of $84.268(3)^\circ$. Each ligand molecule forms two five-membered ring upon coordination to the Co(III) cation. The rings Co/C/C/N/O and Co/S/C/N/N formed by each ligand are almost planar and form a dihedral angle of $7.087(1)^\circ$ and $4.356(1)^\circ$, respectively, showing a slight twist in the ligand molecules. The bite angles are $82.08(10)^\circ$ and $87.02(8)^\circ$ for one ligand and for the second ligand molecule $81.33(9)^\circ$ and $87.24(7)^\circ$ showing the distortion of the octahedral geometry. The C2-N4 and C8-N5 bond lengths of $1.320(4) \text{ \AA}$ and $1.313(4) \text{ \AA}$ respectively are compatible with the double bond character [48] while the C-S distances of $1.735(3) \text{ \AA}$ and $1.743(3) \text{ \AA}$ differ from the distance observed for the double bond character C=S *ca.* 1.692 \AA [49,50] and approaches single bond character C-S (1.837 \AA) [45,51]. These facts are indicative that the sulfur atoms coordinated with the Co(III) cation in their thiolate form. Therefore, the Co-S distances of $2.1818(8)$ and $2.1843(8) \text{ \AA}$ are shorter than those reported for the complexes $[Co(H_2L)_2]Cl$ where H_2L is 2-[(2-hydroxyphenyl)methylene]hydrazine-*N*-(2-propenyl)carbothioamide [52] and bis[bis(2-hydroxy-3-methoxybenzaldehydethiosemicarbazonato)cobalt(III)]dithio nate-dimethylformamide-methanol [53] in which the sulfur atom coordinated with the Co(III) in its thione form. In the anionic unit $[Co(NSC)_4]^{2-}$, both anionic N-donor thiocyanates are quasi-linear with angle $179.2(4)^\circ$ [N7-C10-S3] and $178.1(4)^\circ$ [N8-C11-S4]. These anionic N-donor thiocyanates bind almost linearly to the cobalt(II) ion with angle Co2-N-CS in the range of $158.2(4)^\circ$ and $169.8(4)^\circ$. The Co2-N distances of $1.955(4) \text{ \AA}$ and $1.942(4) \text{ \AA}$ are in accordance with the values reported for Co-N_{NCS} [54]. The geometry around the

tetracoordinated Co2 cation is determined by the distortion index or the tetragonality parameter [55] $\tau_4 = (360^\circ - \alpha - \beta)/141$ where α and β are the two largest angles around the metal center. The expected values for τ_4 are zero for a perfect square plane and one for a perfect tetrahedron. The value of τ_4 , which is 0.9677 , suggests a slightly distorted tetrahedral geometry around the Co2 cation.

The structure of the complex is consolidated by numerous inter- and intra-molecular hydrogen bonds. The cationic unit, half of the anionic unit, and the free methanol of the asymmetric unit are connected by intramolecular hydrogen bonds of type N_{amino}-H...O_{methanol} (N6-H6B...O3), O_{methanol}-H...S_{NCS} (O3-H3...S3) and C_{Me}-H...S_{NCS} (C7-H7A...S4). Intermolecular hydrogen bond of type O_{alcoholic}-H...N_{hydrazinyl} (O1-H1...N2ⁱ; i = $-x+5/4, y-1/4, z-1/4$); N_{amino}-H...S_{NCS} (N3-H3A...S3ⁱⁱ; ii = $x, y+1/2, z+1/2$); N_{amino}-H...O_{alcoholic} (N3-H3B...O1ⁱⁱⁱ), O_{alcoholic}-H...N_{NCS} (O2-H2...N5ⁱⁱⁱ; iii = $-x+5/4, y+1/4, z+1/4$) and O_{methanol}-H...N_{amino} (O3-H3...N3^{iv}; iv = $x, y-1/2, z-1/2$) and weak intramolecular hydrogen bonds involving C_{Methyl}-H...S_{thione} (C7-H7A...S2ⁱ) and (C3-H3E...S1ⁱⁱⁱ) (i = $-x+5/4, y-1/4, z-1/4$ and iii = $-x+5/4, y+1/4, z+1/4$), C_{Methylene}-H...O_{methanol} (C5-H5B...O3ⁱⁱⁱ); C_{Methanol}-H...N_{hydrazinyl} (C9-H9A...N2^v; v = $-x+1, -y+1, z$) link cationic unit, half of the anionic unit and free methanol belonging to different asymmetric units. The combined hydrogen bonds links give rise to a three-dimensional network architecture (Figure 2, Table 4).

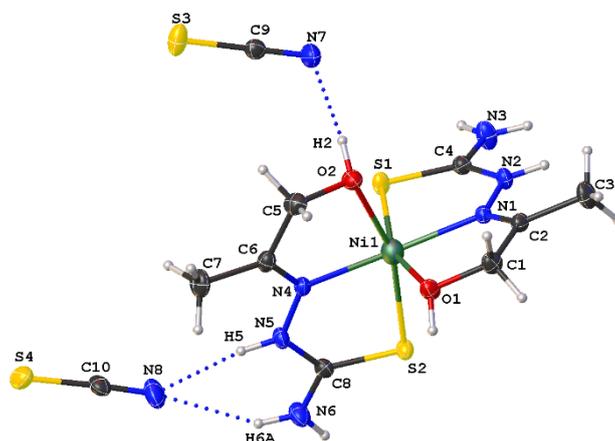
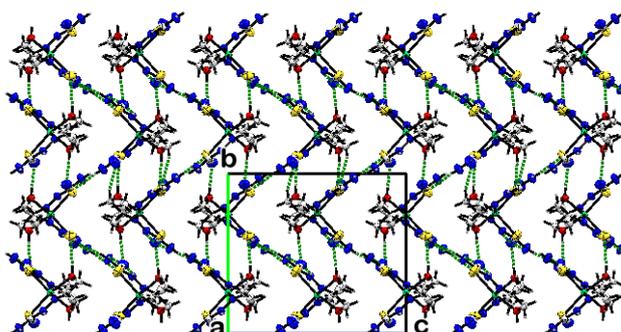
3.2.2. Complex 2

The hexacoordinated mononuclear compound 2 crystallizes in the monoclinic system with the space group $P2_1/n$. The selected bond distances and angles relevant to the coordination sphere of the complex are given in Tables 2 and 3, respectively. The ORTEP representation of complex 2 formulated as $\{[Ni(H_2L)_2] \cdot [(NCS)_2]\}$ is shown in Figure 3. The asymmetric unit contains two neutral molecules ligands, one Ni(II) cation, and two free thiocyanate anions. The metal atom is situated in a $N_2O_2S_2$ inner.

Table 5. Hydrogen-bond geometry (Å, °) for complex 2.

D	H	A	D-H	H...A	D-A	∠ D-H...A
O1	H1	S4 ⁱ	0.871(9)	2.339(9)	3.1990(16)	169.5(17)
O2	H2	N7	0.867(9)	1.942(10)	2.806(3)	174(2)
N2	H2A	N7 ⁱⁱ	0.86	2.15	2.941(2)	153.2
N5	H5	N8	0.86	2.07	2.882(3)	157.8
N3	H3A	N7 ⁱⁱ	0.86	2.30	3.066(3)	148.9
N3	H3B	N8 ⁱⁱⁱ	0.86	2.30	3.158(3)	171.7
N6	H6A	N8	0.86	2.42	3.162(3)	144.6
N6	H6B	S3 ^{iv}	0.86	2.54	3.390(2)	170.1
C1	H1A	S2 ^v	0.97	2.97	3.898(2)	161.3

Symmetry codes: (i) $-x+1, -y+2, -z+1$; (ii) $-x+2, -y+1, -z+1$; (iii) $-x+3/2, y-1/2, -z+3/2$; (iv) $x+1/2, -y+3/2, z+1/2$; (v) $-x+2, -y+2, -z+1$.

**Figure 3.** Single crystal structure of complex 2.**Figure 4.** Packing diagram of complex 2 viewed along the *a*-axis.

Each η^3 -H₂L ligand acts in tridentate fashion through its azomethine nitrogen atom, alcoholic oxygen atom and sulfur atom. The environment around the Ni(II) cation is best described as a strongly distorted octahedral geometry. The equatorial plane is occupied by S1, N4, O1 and N1 with *transoid* angle values of 169.08 (6) and 160.09 (4)° and *cisoid* angle values in the range 77.71(6)-104.76(5)°. The angle subtended by the atoms S2 and O2 that occupied the apical positions is 161.09(4)°. All the angle around the Ni(II) cation deviate severely from the ideal values of 90° and 180° expected for a perfect octahedral geometry. Each ligand form two five membered rings which are almost planar [Ni/S/C/N/N (rms: 0.842 Å and 0.0740 Å) and NiNCCO (rms: 0.0956 Å and 0.0440 Å)]. In each ligand molecule, the two five membered rings issued from the coordination form dihedral angles of 10.606(1)° and 8.592(1)°, respectively. The bite angles values in the five membered rings are in the range 77.71(6)°-83.40(5)°. These observations confirm the severely distorted octahedral geometry around the Ni(II) cation. The two free anionic thiocyanate groups are quasi-linear with an angle N-C-S of 176.1(2)° and 179.6(2)°. The Ni-O bond lengths of 2.1234(14) Å and 2.1240(14) Å are almost equal and are

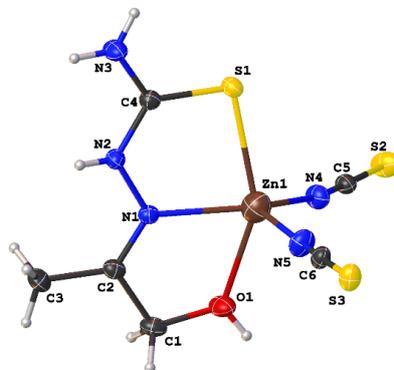
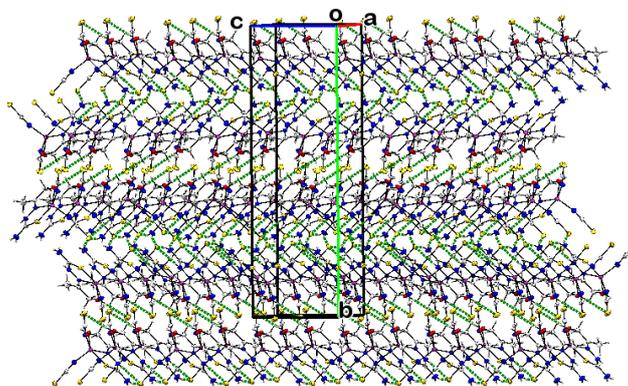
comparable to the similar complex reported by Netalkar *et al.* [34]. The Ni-S distances (2.3983(5) Å and 2.3867(5) Å) and the C-S distances (1.69 (2) Å and 1.695(2) Å) are indicative that the sulfur atom link to Ni atom in thione form [34]. In fact, the C-S distances are comparable to the corresponding distances and the Ni-S distances and are in the range found for the complex [NiLCl] (where L is 2-acetylpyridine-4-*N-p*-chlorophenylthio semicarbazone) in which the sulfur atom link to the nickel(II) in its thione form [34].

Intramolecular hydrogen bonds of type O_{alcoholic}-H...N_{NCS} (O2-H2...N7), N_{hydrazinyl}-H...N_{NCS} (N5-H5...N8) and N_{amino}-H...N_{NCS} (N6-H6A...N8). Intermolecular hydrogen bond of type O_{alcoholic}-H...N_{NCS} (O1-H1...S4ⁱ; i = $-x+1, -y+2, -z+1$); N_{hydrazinyl}-H...N_{NCS} and N_{amino}-H...N_{NCS} (N2-H2A...N7ⁱⁱ; ii = $-x+2, -y+1, -z+1$), N_{amino}-H...N_{NCS} (N3-H3A...N7ⁱⁱ; ii = $-x+2, -y+1, -z+1$ and N3-H3B...N8ⁱⁱⁱ; iii = $-x+3/2, y-1/2, -z+3/2$), O_{alcoholic}-H...N_{NCS} (O2-H2...N5ⁱⁱⁱ; iii = $-x+5/4, y+1/4, z+1/4$) and N_{amino}-H...S_{thione} (N6-H6B...S3^{iv}; iv = $x+1/2, -y+3/2, z+1/2$) and weak intramolecular hydrogen bonds involving C_{Methylene}-H...S_{thione} (C1-H1A...S2^v; v = $-x+2, -y+2, -z+1$) link the molecules into three-dimensional network architecture (Figure 4, Table 5).

Table 6. Hydrogen-bond geometry (Å, °) for complex 3.

D	H	A	D-H	H...A	D-A	∠D-H...A
N3	H3A	S3 ⁱ	0.85(2)	2.69(3)	3.482(2)	154(2)
N3	H3B	S3 ⁱⁱ	0.82(3)	2.71(3)	3.507(2)	164(2)
N2	H2	S3 ⁱ	0.79(2)	2.62(2)	3.3799(17)	160(2)
O1	H1	S2 ⁱⁱⁱ	0.76(3)	2.49(3)	3.2435(17)	173(3)

Symmetry codes: (i) $x, y, z+1$; (ii) $x-1, -y+3/2, z+1/2$; (iii) $x+1, y, z$.

**Figure 5.** Single crystal structure of complex 3.**Figure 6.** Packing diagram of complex 3 viewed along the *b*-axis.

3.2.3. Complex 3

The penta-coordinated mononuclear compound **3** crystallizes in the monoclinic system with the space group $P2_1/c$. The selected bond distances and angles relevant to the coordination sphere of the complex are given in Tables 2 and 3, respectively. The ORTEP representation of the complex (**3**) formulated as $[Zn(H_2L)(NCS)_2]$ is shown in Figure 5. The complex **3** is built up as a mononuclear. The asymmetric unit contains one Zn(II) ion, one neutral η^3 - H_2L ligand acting in tridentate fashion, and two η^1 -thiocyanate anions coordinated through the nitrogen atom to the metal center. The geometry around the Zn(II) is best discussed with the trigonality parameters. The Addison index [56] $\tau = (\beta - \alpha)/60$ in which β and α represent the largest angle around the metal center is frequently used to determine the type of environment around the metal center. A perfect trigonal bipyramidal geometry is obtained when the τ value is 1, while a τ value of zero define a perfect square pyramidal geometry. In the penta-coordinated Zn(II) complex the τ value of 0.2403 is indicative of a strongly distorted square pyramidal geometry around the Zn(II) ion. However, the modified index suggested by Konno *et al.* [57] $\chi = (\beta + \gamma + \delta - 2\alpha)/180$ (which takes into account the other angles β and α are the largest angles, γ and δ are the other angles around the metal centers without the donor atoms defining β) is used, the χ value of 0.5603 suggests that the geometry around the zinc (II) atom is a strongly distorted trigonal bipyramid. The equatorial plane of the

trigonal bipyramid is occupied by three nitrogen atoms N1, N4 and N5. The distortion of the geometry is indicated by the angle values subtended by the N1, N4, and N5 atoms [$N4-Zn1-N1 = 135.67(7)^\circ$; $N5-Zn1-N1 = 107.54(7)^\circ$ and $N4-Zn1-N5 = 114.48(8)^\circ$], which deviates severely from the ideal value of 120° . The sum of these angle values of 357.69 deviates from the ideal value of 360° . The apical position are occupied by the sulfur S1 atom of the semicarbazide moiety and the alcoholic oxygen atom with angle value of $150.09(5)^\circ$ [$O1-Zn1-S1$] severely deviated from the ideal value of 180° . The whole anionic N-donor thiocyanate groups are quasi-linear with angle values $N4-C5-S2 = 179.14(18)^\circ$ and $N5-C6-S3 = 178.31(19)^\circ$. These anionic N-donor thiocyanate do not bind linearly to the zinc (II) ion with Zn-N-CS angle values of $168.74(18)$ and $169.45(18)^\circ$. The tridentate ligand forms two five-membered rings $Zn1/O1/C1/C2/N1$ and $Zn1/S1/C4/N2/N1$ that share one vertex (N1). The atoms of the rings are quite coplanar with respective rms of 0.821 \AA and 0.0432 \AA . The mean planes defined by $Zn1/O1/C1/C2/N1$ and $Zn1/S1/C4/N2/N1$ form a dihedral angle of $9.351(1)^\circ$. The atoms situated in the basal plane $N1N4N5Zn1$ are quite coplanar. The Zn1 is displaced from the plane defined by the remaining three atoms by about $0.1291(8) \text{ \AA}$. The basal plane form with the mean planes of rings dihedral angle of $87.082(1)^\circ$ ($Zn1S1C4N2N1$) and $83.746(5)^\circ$ ($Zn1O1C1C2N1$). The nitrogen atoms of the η^1 -thiocyanate groups are strongly linked to the Zn(II) atom as shown by the bond length values of $1.9576(16) \text{ \AA}$ [$Zn1-N4$] and $1.9743(18) \text{ \AA}$

[Zn1-N5]. These values are comparable to those reported for a similar complex [58,59]. These lower values, compared to the value 2.0973 (15) [Zn1-N1], are due to the anionic character of N4 and N5 of the thiocyanate group, contrary to the neutrality of N1 from the Schiff base. The sulfur atom and the alcoholic oxygen atom that occupy the apical positions are slightly linked to the zinc (II) atom as shown by the distance values of Zn1-S1 = 2.4335(5) Å and Zn-O1 = 2.1846(16) Å. These values are in accordance with those found for similar complexes in which sulfur and oxygen act in nonanionic form [60-62]. No intramolecular hydrogen bond is present in the zinc complex. Intermolecular hydrogen bond of type $N_{\text{amino}}\text{-H}\cdots\text{S}_{\text{NCS}}$ and $N_{\text{hydrazinyl}}\text{-H}\cdots\text{S}_{\text{NCS}}$ ($N3\text{-H3A}\cdots\text{S3}^i$ and $N2\text{-H2}\cdots\text{S3}^i$; $i = x, y, z+1$), $N_{\text{amino}}\text{-H}\cdots\text{S}_{\text{NCS}}$ ($N3\text{-H3B}\cdots\text{S3}^{ii}$; $ii = x-1, -y+3/2, z+1/2$), $O_{\text{alcoholic}}\text{-H}\cdots\text{S}_{\text{NCS}}$ ($O1\text{-H1}\cdots\text{S2}^{iii}$; $iii = x+1, y, z$) link the molecules into three-dimensional network architecture (Figure 6, Table 6).

4. Conclusions

Compounds **1**, **2** and **3** synthesized using the ligand 1-(1-hydroxypropan-2-ylidene)thiosemicarbazide (H₂L) and were characterized with various physicochemical techniques such as elemental analyses, IR and single crystal X-ray diffraction analysis. The complex **1** is formed with one cationic unit containing Co(III) ion and one half anionic unit containing Co(II) ion. Two deprotonated ligand molecules acting in a tridentate fashion coordinate the Co(III) ion, yielding the cationic unit. The anionic unit is formed by a tetrathiocyanate cobalt moiety in which the cobalt(II) center is located on the crystallographic two fold axis of the *Fdd2* space group and accounts for only ½ in the asymmetric unit. The Co(III) and the Co(II) metal centers are, respectively, situated in octahedral and tetrahedral environments. In Complex **2**, the Ni(II) ion is coordinated by two neutral ligand molecules that act in a tridentate fashion, yielding an octahedral geometry around the nickel(II) center. Two uncoordinated thiocyanate anions are present. In complex **3**, the zinc(II) center is coordinated by one neutral ligand molecule and two thiocyanate anions through their nitrogen atoms. The geometry around the Zn(II) center is best described as a distorted trigonal bipyramid environment.

Supporting information

CCDC-2155588, 2155703 and 2155587 contain the supplementary crystallographic data for complexes **1**, **2** and **3**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest. Ethical approval: All ethical guidelines have been adhered. Sample availability: Samples of the compounds are available from the author.

CRedit authorship contribution statement

Conceptualization: Mohamed Gaye, Ousmane Diouf; Methodology: Mohamed Gaye, Ousmane Diouf, Mamadou Sidibé; Software: Cheikh Ndoye, Gregory Excoffier, Ibrahima Elhadji Thiam; Validation: Mohamed Gaye, Ousmane Diouf, Mamadou Sidibé; Formal Analysis: Cheikh Ndoye, Gorgui Awa Seck; Investigation: Cheikh Ndoye, Gorgui Awa Seck; Data Curation: Cheikh Ndoye, Gorgui Awa Seck; Writing - Original Draft: Mohamed Gaye, Ousmane Diouf; Writing - Review and Editing: Mohamed Gaye; Visualization: Cheikh Ndoye, Gregory Excoffier, Ibrahima Elhadji Thiam; Supervision: Mohamed Gaye, Ousmane Diouf.

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