

The Effect of Azide and Thiocyanate Anions on the Coordination Mode of Thiocarbohydrazone Ligand in Preparing Mn(II) Coordination Compounds

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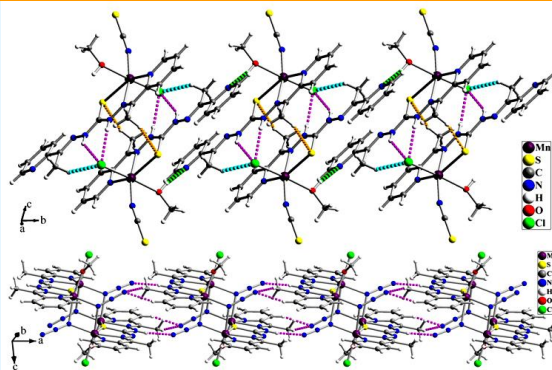
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Abstract: Two new Mn(II) coordination compounds, [Mn(HL)(NCS)(Cl)(CH₃OH)] (**1**) and [Mn₄(L)₂(μ-N₃)₄(N₃)_{0.5}(Cl)_{1.5}(CH₃OH)₂]·3.5(CH₄O) (**2**), were synthesized and characterized by elemental analysis and spectroscopic methods where HL is bis-[(*E*)-*N'*-(methyl(pyridin-2-yl)methylene)]thiocarbohydrazone.

The compounds were synthesized by the reaction of HL, MnCl₂·4H₂O and KSCN (in **1**) or NaN₃ (in **2**) with 1:2:4 molar ratios in methanol. The crystal structures of **1** and **2** were determined by single-crystal X-ray diffraction analysis which revealed that **1** is a mononuclear Mn(II) coordination compound while **2** is an azido bridged tetranuclear Mn(II) cluster. In both **1** and **2** the Mn(II) ions have octahedral coordination environment which is created by coordination of nitrogen and sulfur atoms from thiocarbohydrazone ligand. In compound **1** the ligand acts as a neutral tridentate N₂S-donor ligand while in **2** it acts as mononegative N₄S-donor ligand. In **2**, the azide anions act as both terminal and bridging ligand and four Mn(II) ions are connected together by four bridging azide ligands. Furthermore, the Mn(II) ions in **2** are also connected together by sulfur atoms of the thiocarbohydrazone ligand. The FT-IR spectra of **1** and **2** show the characteristic bands of SCN⁻ and N₃⁻ anions, respectively. The analysis indicated that the pseudo-halide SCN⁻ and N₃⁻ anions have considerable effect on the structure and nuclearity of the coordination compounds. The formation of tetranuclear cluster in the presence of azide anion was attributed to its higher ability to act as bridging group and also its relatively basic character which influence on the coordination mode of the thiocarbohydrazone ligand.



Keywords: Mn(II) coordination compounds, Crystal structure, Spectroscopic studies, Thiocarbohydrazone, Azide and thiocyanate

1. INTRODUCTION

The design and synthesis of new coordination compounds is still one of the important research fields in synthetic inorganic and coordination chemistry.¹ This is mainly related to the widespread applications of coordination compounds in various fields and also their diverse structural properties.² There is also continuous interest in the coordination chemistry of manganese ion by considering its occurrence in several biological systems (like in the active centre of oxygen-evolving complex (OEC) in Photosystem II,³ in Mn-containing superoxide dismutase (Mn-SOD),⁴ etc.) and also its applications in catalytic⁵ and magnetic⁶ systems. Manganese coordination compounds have been widely used as useful models for studying metalloenzymes and mimicking several biological systems.⁷ Manganese coordination compounds by having large numbers of unpaired electrons in various

oxidation states are also attractive and important materials for studying the magnetic exchange interactions.⁸

The pseudo-halide anions (N₃⁻, SCN⁻, OCN⁻, CN⁻, N(CN)₂⁻, etc.) are attractive ligands in coordination chemistry because they can act as bridging ligands between metal ions to form multinuclear coordination compounds and coordination polymers.⁹ They can also act as terminal monodentate ligand and control the charge balance depending on the structural, steric and electronic requirements.¹⁰ These anions also play an important role in the magnetic exchange interactions when act as bridging ligand between paramagnetic metal ions.¹¹ Although pseudo-halides are generally powerful bridging ligands and in some cases they have close structures, different pseudo-halides have completely independent, unique and sometimes unpredictable behavior in the same reaction condition. Therefore, changing pseudo-halides in the same reaction condition usually gives completely different

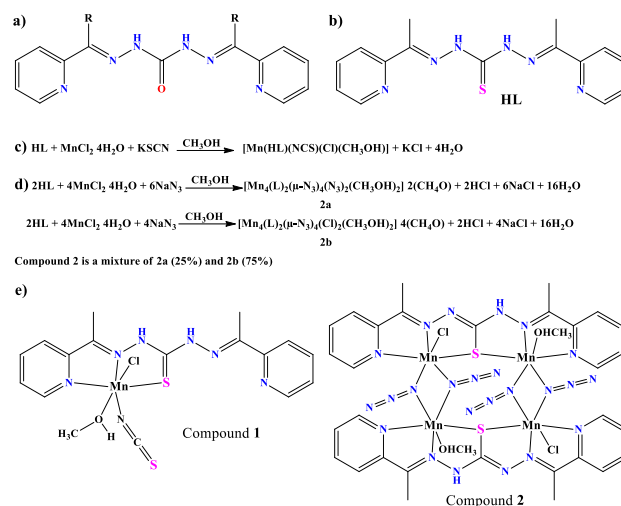
products.¹² Due to this, several studies have been done to the use of various organic ligands with these bridging groups to find the effective parameters in their coordination modes.

Thiocarbohydrazone ligands obtained by the reaction of thiocarbohydrazide with 2-pyridylketones are symmetric multidentate ligands in hydrazone family. They are quite similar to carbohydrazone ligands (Scheme 1a) and can be considered as their sulfur donor analogues because only C=O is changed to C=S (see Scheme 1). Carbo- and thiocarbohydrazone ligands by having several donor atoms in suitable positions are ideal precursors for designing multinuclear transition metal coordination compounds. They usually coordinate to two metal ions through dicompartmental N₂O-/N₂S-donor groups which the central oxygen or sulfur atom usually acts as bridging atom between two metal ions.¹³ Although several structures with carbohydrazone ligands have been reported in Cambridge Crystallographic Data Center (CCDC),¹⁴ there is seldom report for thiocarbohydrazones. Previous reports indicate both carbo- and thiocarbo-hydrazones can form [2×2] tetranuclear grid complexes with transition metal ions like Fe,¹⁵ Co,¹⁶ Ni,¹⁷ Cu¹⁸ and Zn¹⁹ ions. Although using a mixture of carbo- or thiocarbo-hydrazones with pseudo-halides can give interesting coordination compounds, there is no considerable report in this area. We have previously reported the structure of Mn(II)²⁰ and Cr(III)²¹ coordination compounds of carbohydrazones with azide and dicyanamide. Some lanthanides coordination compounds with carbohydrazone and azide ligands have been also reported in literature.²² Nevertheless, there is no report on the use of mixture thiocarbohydrazones and pseudo-halides. In the present work we report synthesis, characterization, crystal structure and spectroscopic properties of two new Mn(II) coordination compounds with thiocarbohydrazone ligand in the presence of azide and thiocyanate anions (see Scheme 1b-1c). The results indicate that pseudo-halides have considerable effect on the coordination mode of the ligand and the structure of product.

2. EXPERIMENTAL

Materials and instrumentation

Manganese(II) chloride tetrahydrate, 2-acetylpyridine, sodium azide and potassium thiocyanate were purchased from Merck and used as received without further purification. Thiocarbohydrazide was provided from Alfa Aesar. The ligand bis-[(*E*)-*N'*-(methyl(pyridin-2-yl)methylene)]thiocarbohydrazide (HL) was synthesized and characterized according to our previous report.²³ FT-IR spectra were recorded by using Bruker FT-IR spectrophotometer as KBr disks. Elemental analyses were carried out using a Perkin-Elmer 240 elemental analyzer. UV-Vis spectra of solutions were recorded on a thermo analysis for determining the manganese content of the compounds was carried out using Varian Spectra AA-220 equipment.



Scheme 1. a) General structure of carbohydrazones; b) the structure of HL; chemical formula for the synthesis of c) compound 1 and d) compound 2; e) schematic structure of compounds 1 and 2

Synthesis of [Mn(HL)(NCS)(Cl)(CH₃OH)] (1)

Compound 1 was synthesized by the reaction of thiocarbohydrazone ligand, HL, (0.312 g, 1.0 mmol), MnCl₂·4H₂O (0.396 g, 2.00 mmol) and KSCN (0.389 g, 4.00 mmol) in 30 mL methanol. HL was dissolved in methanol and KSCN was added to it. Then, MnCl₂·4H₂O was added to the solution. The mixture was refluxed for 12 hours and the color of solution was slowly changed to yellow. Then, the volume of solvent was decreased to 5 mL and the reaction flask was cooled to room temperature. The resulting yellow precipitates were isolated by filtration and washed by cold methanol. The single crystals of compound 1 were obtained by recrystallization of the final product in methanol. Yield based on HL: 76% (0.187 g). *Anal. Calc.* for C₁₇H₂₀ClMnN₇O₅S₂ (MW = 492.91): C, 41.42; H, 4.09; N, 19.89; Mn, 11.15%. *Found:* C, 41.48; H, 4.06; N, 19.93; Mn, 11.21%. FT-IR (KBr, cm⁻¹): 3425 (s, br), 3166 (m, br), 3143 (m, br), 3097 (w), 2924 (w), 2080 (vs), 2067 (vs), 1613 (m), 1594 (m), 1581 (w), 1546 (vs), 1471 (s), 1438 (s), 1376 (m), 1334 (w), 1306 (m), 1295 (m), 1255 (s), 1203 (m), 1152 (w), 1097 (m), 1071 (s), 1012 (s), 999 (s), 902 (w), 799 (s), 783 (vs), 759 (w), 744 (w), 664 (m), 630 (m), 610 (w), 565 (w), 475 (w), 438 (w), 401 (s). UV-Vis (in CH₃OH, c = 5 × 10⁻⁵ mol dm⁻³, λ_{max} [nm] with ε [M⁻¹ cm⁻¹]): 216 (27100), 394 (22700) and 500 nm (17900).

Synthesis of [Mn₄(L)₂(μ-N₃)₄(N₃)_{0.5}(Cl)_{1.5}(CH₃OH)₂]·3.5(CH₃OH) (2)

Compound 2 was synthesized by similar procedure as compound 1 and only sodium azide was used instead of KSCN. Red precipitates of compound 2 were obtained by refluxing a mixture of HL, (0.312 g, 1.0 mmol), MnCl₂·4H₂O (0.396 g, 2.00 mmol) and NaN₃ (0.260 g, 4.00 mmol) in methanol. The product was isolated by filtration and it was recrystallized in methanol. Yield based on HL: 76% (0.187 g). *Anal. Calc.* for C_{35.5}H₅₂Cl_{1.5}Mn₄N_{25.5}O_{5.5}S₂ (MW = 1261.08): C, 33.81; H, 4.16; N, 28.32; Mn, 17.43%. *Found:* C, 33.70; H, 4.09; N, 28.54; Mn, 17.51%. FT-IR (KBr, cm⁻¹): 3483 (m, br), 3387 (m), 3211 (m, br),

Table 1. Crystallographic information of compounds **1** and **2**

Compound	1	2
Formula	C ₁₇ H ₂₀ ClMnN ₇ OS ₂	C _{35.5} H ₅₂ Cl _{1.5} Mn ₄ N _{25.5} O _{5.5} S ₂
<i>M</i> /g mol ⁻¹	492.91	1261.08
crystal size/mm	0.34 × 0.12 × 0.11	0.43 × 0.10 × 0.08
T/K	100	100
crystal shape, colour	Block, yellow	Block, red
crystal system	Triclinic	Monoclinic
space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
Absorption correction	Analytical	Analytical
<i>a</i> /Å	8.562(2)	10.798(4)
<i>b</i> /Å	9.789(3)	11.591(5)
<i>c</i> /Å	13.150(4)	21.705(10)
α /°	73.99(3)	90
β /°	83.04(3)	90.66(4)
γ /°	86.38(3)	90
<i>V</i> /Å ³	1051.1(5)	2716(2)
<i>Z</i>	2	2
<i>D</i> _x /Mg m ⁻³	1.557	1.542
μ /mm ⁻¹	0.98	1.13
Measured reflections	17054	14201
Independent reflections	7862	6342
Reflections with <i>I</i> > 2 σ (<i>I</i>)	5463	3988
Parameters	265	353
<i>R</i> _{int}	0.026	0.039
Θ range/°	3.0–36.7	3.2–28.7
<i>T</i> _{min} , <i>T</i> _{max}	0.782, 0.907	0.748, 0.929
<i>h, k, l</i>	–11→14	–12→13
	–11→15	–13→15
	–22→21	–28→28
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)]	0.041	0.039
<i>R</i> _w (<i>F</i> ²)	0.091	0.062
<i>S</i>	1.02	1.01
(Δ / σ) _{max}	< 0.001	0.002
Max electron density/e Å ⁻³	0.76	0.35
Min electron density/e Å ⁻³	–0.47	–0.28

3065 (w), 2922 (w), 2098 (vs), 2069 (vs), 1631 (m), 1598 (s), 1560 (s), 1517 (s), 1470 (s), 1439 (m), 1406 (m), 1363 (m), 1337 (m), 1308 (m), 1291 (m), 1269 (m), 1247 (s), 1208 (s), 1163 (m), 1147 (m), 1097 (m), 1066 (s), 1046 (s), 1015 (m), 897 (w), 831 (w), 792 (s), 736 (s), 703 (m), 655 (m), 643 (m), 607 (m), 553 (m), 485 (w), 464 (w), 413 (m). UV-Vis (in CH₃OH, *c* = 2 × 10⁻⁵ mol dm⁻³, λ_{max} [nm] with ϵ [M⁻¹ cm⁻¹]): 220 (22900), 363 (24700) and 505 nm (16000).

Single crystal X-Ray diffraction data collection and refinement

Single crystal X-ray data collection for compounds **1** and **2** was performed on a KUMA-KM4 diffractometer using ω scans and a graphite-monochromated Mo K α (λ = 0.71073 Å) radiation. The data were collected at 100 K and the details of refinement parameters and a summary of the crystallographic data are given in Table 1. The structure were solved with SHELXS²⁴ and refined with the full-matrix least-squares procedure on *F*² by SHELX-2014.²⁵ All of the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included in idealized geometry riding on their parent atoms with the exception of the N- and O-bonded hydrogen atoms which were at initial stage of refinement located from difference Fourier maps and then constrained with AFIX 3 command.

3. RESULTS AND DISCUSSION

Synthesis and spectroscopy

The symmetric nitrogen and sulfur donor Schiff base ligand, HL, was synthesized by the reaction of thiocarbohydrazide with two equivalents of 2-acetylpyridine according to previous report.²³ In the FT-IR

spectrum of HL the bands at 1585, 3165 and 1118 are attributed to C=N, NH and C=S functional groups.

Reaction of HL, manganese(II) chloride tetrahydrate and potassium thiocyanate in 1:2:4 molar ratios gave a yellow precipitates related to Mn(II) coordination compound, [Mn(HL)(NCS)(Cl)(CH₃OH)] (**1**), according to the reaction presented in Scheme 1c. Compound **1** was obtained as crystalline material by recrystallization of the yellow precipitates in methanol. The same reaction of HL and MnCl₂·4H₂O in the presence of sodium azide with 1:2:4 molar ratios in methanol gave red crystals of compound **2** in a similar procedure. Both of the compounds were investigated by FT-IR spectroscopy. In the FT-IR spectrum of both **1** and **2** the broad bands at about 3450 cm⁻¹ are related to the presence of OH groups and confirm the presence of methanol molecules in the structure of the products.²⁶ The bands at about 3150 cm⁻¹ (3166 and 3143 cm⁻¹ for **1** and 3211 cm⁻¹ for **2**) are related to the N–H vibration of the thiocarbohydrazone ligand.²⁷ Comparing FT-IR spectrum of **1** and **2** with free ligand it is seen that the characteristic bands of ligand are observed in the FT-IR spectra of coordination compounds with slight shifts. This matter confirms the coordination of thiocarbohydrazone ligand to the metal core in both **1** and **2**. The band at about 1600 cm⁻¹ (1594 in **1** and 1598 in **2**) confirm the coordination of imine nitrogen to the metal ion.²⁸ This band is shifted to higher frequencies respect to free ligand. It should be noted that the band at 1613 cm⁻¹ in

the FT-IR spectrum of **1** is related to the free C=N functionality and is a strong evidence for the presence of uncoordinated C=N functionality in the structure of this compound. Also, a new band is observed at 1631 cm^{-1} in the FT-IR spectrum of **2** which can be assigned to the presence of $-\text{C}=\text{N}-\text{N}=\text{C}-$ moiety in the structure of this product.²⁹ There are two new very strong bands in the FT-IR spectra of both **1** and **2** which are absent in the FT-IR spectrum of free ligand. These bands are observed at 2080 and 2067 cm^{-1} in the FT-IR spectrum of **1** which are related to the presence of SCN^- anion in the structure of this compound.³⁰ Also, the very strong bands at 2080 and 2067 cm^{-1} in the FT-IR spectrum of **2** can be attributed to the presence of the coordinated terminal and bridging azide anions to the manganese ion, respectively.³¹

UV-Vis spectrum of HL and compounds **1** and **2** in methanol are shown in Figure 1. The UV-Vis spectrum of HL shows three bands at 214, 328 and 416 nm, which are attributed to $\pi \rightarrow \pi^*$ (214 nm) and $n \rightarrow \pi^*$ (328 and 416 nm) transitions. The UV-Vis spectrum of compound **1** shows three bands at 216, 394 and 500 nm.³² The band at 216 nm is related to intraligand $\pi \rightarrow \pi^*$ transitions. The broad band at 394 nm is related to a mixture of intraligand $n \rightarrow \pi^*$ transitions and also ligand to metal charge transfer (LMCT). The change in the position, shape and intensity of this band can be attributed to the coordination of nitrogen and sulfur atoms to the metal core. The broad absorbance band at about 500 nm is observed as a new band in the UV-Vis spectrum of **1** which is mainly due to the ligand to metal charge transfer (LMCT) transitions.³³ The UV-Vis spectrum of compound **2** is also similar to compound **1** and has three bands at 220, 363 and 505 nm which can be attributed to intraligand $\pi \rightarrow \pi^*$ (220 nm) and also $n \rightarrow \pi^*$ and LMCT transitions (363 and 505 nm).

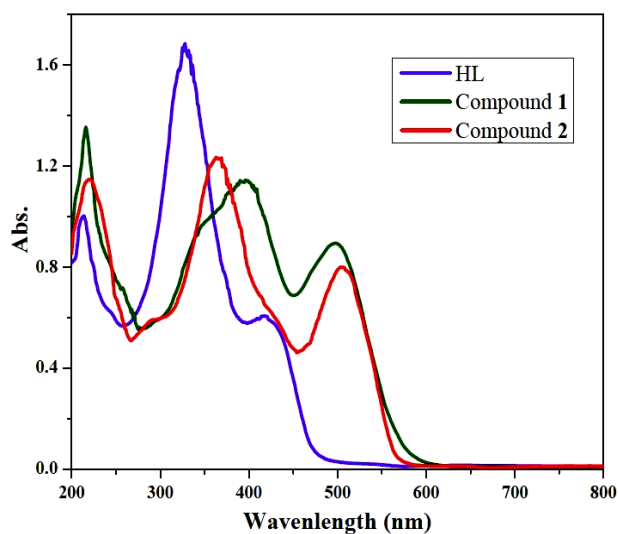


Figure 1. UV-Vis spectra of HL, compound **1** and compound **2** in methanol

Crystal structure of $[\text{Mn}(\text{HL})(\text{NCS})(\text{Cl})(\text{CH}_3\text{OH})]$ (**1**)

The yellow crystals of the compound **1** crystallize in $P-1$ space group. Figure 2 shows the molecular structure of compound **1** and selected bond lengths and angles are given in Table 2. According to the results of X-ray analysis compound **1** is a mononuclear Mn(II) coordination compound which is comprised of thiocarbohydrazone ligand, thiocyanate ion and chloride ion attached to the manganese(II) ion. The coordination geometry around Mn(II) ion can be described as distorted octahedral geometry. The ‘ MnClN_3SO ’ coordination environment in compound **1** is created by sulfur and two nitrogen atoms from HL, as well as a nitrogen atom from thiocyanate anion, chloride anion, and an oxygen atom from coordinated methanol molecule. The ligand is a non-deprotonated tridentate N_2S -donor neutral ligand. The nitrogen atom of one pyridine ring, the imine nitrogen and the thioamidic nitrogen atoms are not coordinated to the metal ion. The N_2S -donor atoms of the organic ligand and the nitrogen atom of SCN^- anion lie in the equatorial plane of the octahedral geometry. The axial positions are occupied by chloride ion and oxygen atom of methanol molecule. The Mn–Cl, Mn–N and Mn–O bond lengths are in the typical range observed for Mn(II) coordination compounds.³⁴ The $\text{N7}-\text{C17}-\text{S2}$ ($178.63(17)^\circ$) and $\text{C17}-\text{N7}-\text{Mn}$ ($165.50(15)^\circ$) angles are almost linear which correspond to the values for the N-coordinated thiocyanate ligand.³⁵ Hydrogen bond interactions are observed due to the presence of NH and OH groups along with Cl, S as well as uncoordinated nitrogen atoms in the structure of **1** (see Figure 3 and Table 3). The OH group of coordinated methanol molecule forms intermolecular $\text{O}-\text{H}\cdots\text{N}$ interaction with the nitrogen atom of uncoordinated pyridine fragment from the neighboring molecule of compound **1**. Also, two NH moieties ($\text{N3}-\text{H3}$ and $\text{N4}-\text{H4}$) of the ligand are involved in intermolecular $\text{N}-\text{H}\cdots\text{Cl}$ bifurcated hydrogen bond interaction with chloride anions of neighboring molecules. A 1D polymeric chain is generated by these intermolecular interactions stretching along b crystallographic axis. Moreover, the $\text{C}-\text{H}\cdots\text{Cl}$, $\text{O}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\text{S}$ interactions between adjacent molecules are observed, from which the $\text{C3}-\text{H3}\cdots\text{S2}$ hydrogen bonds connect the 1D chains.

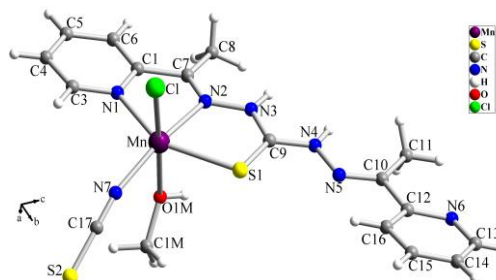


Figure 2. Molecular structure of compound **1** with atom numbering scheme.

Table 2. Selected bond lengths and angles in the crystal structure of compound **1**

Bond	Length/Å	Bond	Angle/°
Mn–N7	2.1070(16)	N7–Mn–N1	108.32(6)
Mn–N1	2.2406(14)	N7–Mn–N2	163.25(5)
Mn–N2	2.3107(15)	N1–Mn–N2	69.98(5)
Mn–O1M	2.3558(15)	N7–Mn–O1M	83.90(6)
Mn–Cl	2.5495(11)	N1–Mn–O1M	88.22(5)
Mn–S1	2.5765(9)	N2–Mn–O1M	79.41(5)
C9–S1	1.6821(17)	N7–Mn–Cl	91.95(5)
N3–C9	1.361(2)	N1–Mn–Cl	94.14(4)
C9–N4	1.352(2)	N2–Mn–Cl	104.77(5)
S2–C17	1.6249(18)	O1M–Mn–Cl	175.70(3)
C17–N7	1.155(2)	N7–Mn–S1	105.43(5)
		N1–Mn–S1	145.41(4)
		N2–Mn–S1	75.53(4)
		O1M–Mn–S1	88.00(4)
		Cl–Mn–S1	92.06(3)
		N7–Cl17–S2	178.63(17)
		C17–N7–Mn	165.50(15)

Table 3. Information of hydrogen bond interactions in the crystal structure of **1** and **2**

D–H...A	D–H	H...A	D...A	D–H...A
Compound 1				
N3–H3A...Cl ⁱ	0.88	2.38	3.1544(18)	147
N4–H4A...Cl ⁱ	0.88	2.39	3.1472(17)	145
O1M–H1M...N6 ⁱⁱ	0.84	2.00	2.809(2)	163
C3–H3...S2 ⁱⁱⁱ	0.95	2.77	3.598(2)	147
Compound 2				
N3–H3A...N3A ⁱ	0.88	2.30	3.156(3)	163
O1M–H1M...O2M	0.84	1.83	2.655(3)	169
O2M–H2M...N1C	0.84	2.21	3.031(15)	166
O2M–H2M...Cl1	0.84	2.26	3.076(2)	164
O3M–H3M...Cl1	0.84	2.40	3.202(4)	159
O4M–H4M...Cl1	0.84	2.18	3.016(7)	173
C6–H6...N3B ⁱⁱ	0.95	2.44	3.342(3)	158
C8–H8B...N3B ⁱⁱ	0.98	2.58	3.523(3)	162

Symmetry codes for **1**: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, -y+2, -z+1$; (iii) $-x+2, -y+1, -z$. For crystal **2**: (i) $-x+2, -y+1, -z+1$; (ii) $x+1, y, z$.

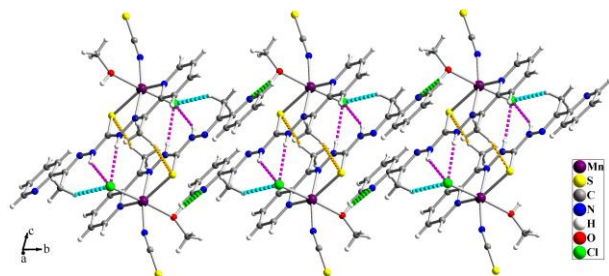


Figure 3. 1D chain obtained by intermolecular hydrogen bond interactions in the crystal structure of compound **1**. The intermolecular interactions are shown as pink (N–H...Cl), green (O–H...N), blue (C–H...Cl) and yellow (C–H...S) dashed lines.

Crystal structure of $[\text{Mn}_4(\text{L})_2(\mu\text{-N}_3)_4(\text{N}_3)_{0.5}(\text{Cl})_{1.5}(\text{CH}_3\text{OH})_2] \cdot 3.5(\text{CH}_4\text{O})$ (**2**)

The red crystals of compound **2** crystallize in $P2_1/n$ space group. The molecular structure of **2** is shown in Figure 4 and selected bond lengths and angles around metal ions are collected in Table 4. Diffraction studies indicated that **2** is a centrosymmetric tetranuclear Mn(II) coordination compound of the pseudo-parallelgram geometry. In the tetranuclear cluster the thiocarbohydrazone ligand is coordinated to two Mn(II) ions together with azide and chloride anions as well as methanol molecules. These two Mn(II) ions in the asymmetric unit are joined by S atom of the ligand forming a side of the parallelgram. The Mn1...Mn2 distance through sulfur bridge equals 5.0345(17) Å and the Mn1–S1–Mn2 angle is 159.94(3)°.

These dinuclear units within the cluster are combined by four azide bridging ligands. The Mn1...Mn2ⁱ distance through the azide bridges is 3.4458(17) Å and the Mn1–N1A–Mn2ⁱ, Mn1–N1B–Mn2ⁱ, N1A–Mn1–N1B and N1B–Mn2ⁱ–N1A angles are 101.86(8), 100.83(8), 77.79(8) and 76.40(7), respectively. Four Mn(II) ions have a distorted octahedral arrangement with Mn1–Mn2–Mn1 and Mn2–Mn1–Mn2 angle of 84.255(13), 95.745(14)°, respectively. The Mn1...Mn1ⁱ and Mn2...Mn2ⁱ distances on the diagonal of the square are 5.8098(19) and 6.380(2) Å, respectively. The Mn1 atom has MnN₄OS coordination environment which is created by coordination of two nitrogen and sulfur atoms from organic ligand, two nitrogen atoms from two bridging azide ligands and oxygen atom from coordinated methanol molecule. Three donor atoms of the thiocarbohydrazone ligand and one of the azide anions form the equatorial plane of octahedral geometry around Mn1 and the axial positions are occupied by methanol molecule and the second azide bridging ligand. The Mn2 ion has similar arrangement to Mn1 but only one axial position is occupied with different ligand. Similar to Mn1, two nitrogen and sulfur atoms of the ligand together with two bridging azide ligands fill five positions of the octahedral geometry. The remaining site is occupied mutually with two different ligands. Chloride anion or terminal azide ligand coordinates to this axial site with s.o.f. = 0.75 (Cl) and 0.25 (N₃), respectively. When Cl atom

Table 4. Selected bond length and angles in the crystal structure of compound **2**

Bond	Length/Å	Bond	Angle/°
Mn1–O1M	2.1681(18)	N1B–Mn1–O1M	90.54(7)
Mn1–N1	2.235(2)	N1B–Mn1–N1	100.86(8)
Mn1–N1A	2.264(2)	O1M–Mn1–N1	94.16(8)
Mn1–N2	2.268(2)	N1B–Mn1–N1A	77.79(8)
Mn1–S1	2.5377(11)	O1M–Mn1–N1A	168.00(7)
Mn2–N1C	2.108(13)	N1–Mn1–N1A	85.50(8)
Mn2–N1A ⁱ	2.174(2)	N1B–Mn1–N2	167.25(7)
Mn2–N6	2.231(2)	O1M–Mn1–N2	100.24(7)
Mn2–N5	2.254(2)	N1–Mn1–N2	71.78(8)
Mn2–N1B ⁱ	2.314(2)	N1A–Mn1–N2	91.07(7)
Mn2–Cl1	2.5055(16)	N1B–Mn1–S1	111.18(6)
Mn2–S1	2.5753(11)	O1M–Mn1–S1	89.30(6)
S1–C9	1.732(2)	N1–Mn1–S1	147.75(6)
C1–N1	1.365(3)	N1A–Mn1–S1	97.41(6)
C1–C6	1.392(3)	N2–Mn1–S1	76.04(6)
C1–C7	1.479(3)	N1A ⁱ –Mn2–N6	110.46(7)
N1–C3	1.336(3)	N1A ⁱ –Mn2–N5	166.18(7)
C3–C4	1.379(3)	N6–Mn2–N5	72.81(7)
Mn1–Mn2	5.0348(17)	N1A ⁱ –Mn2–N1B ⁱ	76.39(7)
Mn1–Mn2 ⁱ	3.4466(16)	N6–Mn2–N1B ⁱ	86.52(8)
Mn1–Mn1 ⁱ	5.8098(19)	N5–Mn2–N1B ⁱ	90.61(7)
Mn2 ⁱ –Mn2 ⁱ	6.380(2)	N1A ⁱ –Mn2–Cl1	93.72(6)
S1–C9	1.732(2)	N6–Mn2–Cl1	88.62(6)
C9–N4	1.322(3)	N5–Mn2–Cl1	99.84(6)
N3–C9	1.379(3)	N1B ⁱ –Mn2–Cl1	166.63(6)
N2–N3	1.366(3)	N1A ⁱ –Mn2–S1	100.27(6)
N4–N5	1.381(2)	N6–Mn2–S1	147.32(5)
		N5–Mn2–S1	74.72(6)
		N1B ⁱ –Mn2–S1	90.24(6)
		Cl1–Mn2–S1	100.50(5)
		Mn1–S1–Mn2	159.94(3)
		Mn2 ⁱ –N1A–Mn1	101.87(8)
		Mn1–N1B–Mn2 ⁱ	100.82(8)
		N1A–N2A–N3A	177.7(2)
		N1B–N2B–N3B	179.4(3)
Bond	Angle/°		
N1C–Mn2–S1	94.6(4)		
N1C–Mn2–N1A ⁱ	97.7(3)		
N1C–Mn2–N6	92.1(4)		
N1C–Mn2–N5	95.6(3)		
N1C–Mn2–N1B ⁱ	173.0(4)		
N1C–N2C–N3C	176.6(13)		

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

is present, an uncoordinated methanol molecule (disordered into two positions) also interacts via O–H \cdots Cl hydrogen bond. Thus, the crystals of compound **2** can be considered as different complex molecules of formulae of $[\text{Mn}_4(\text{L})_2(\mu\text{-N}_3)_4(\text{N}_3)_2(\text{CH}_3\text{OH})_2]\cdot 2(\text{CH}_4\text{O})$ and $[\text{Mn}_4(\text{L})_2(\mu\text{-N}_3)_4(\text{Cl})_2(\text{CH}_3\text{OH})_2]\cdot 4(\text{CH}_4\text{O})$, which correspond to the existence of these two molecules occupying the crystallographic sites of the unit cell in a 0.75:0.25 ratio (see Scheme 1d). The Mn–O and Mn–N bond lengths are close to the reported Mn(II) complexes with hydrazone ligands.³⁴ The hydrogen atom of one of the NH groups is eliminated during the coordination of ligand to the metal core. Thus, the thiocarbohydrazone ligand is coordinated to the metal ion as mono-negative ligand (L^-) acting as both chelating and bridging $\text{N}_4(\mu\text{-S})$ -donor ligand. Comparison of C9–S1 bond lengths of thiocarbohydrazone ligand in compounds **1** (1.6821(17) Å) and **2** (1.732(2) Å) shows it is longer in **2**, which indicate the coordination of S atom as the thiolate bridging group to Mn(II) ions in **2**. Also, the C9–N4 bond in **2** (1.322(3) Å) is shorter than C–NH– bonds (1.379(3) Å in **2**, 1.352(2) and 1.361(2) Å in **1**), which revealed the presence of $-\text{N}=\text{C}(\text{NH})-\text{S}^-$ moiety in the structure of compound **2**. The N–N–N angles in the azide ligands are in the range of 176.6–179.4°, which are almost linear and are consistent

with those in the previously reported coordinated azide ligands.³⁶

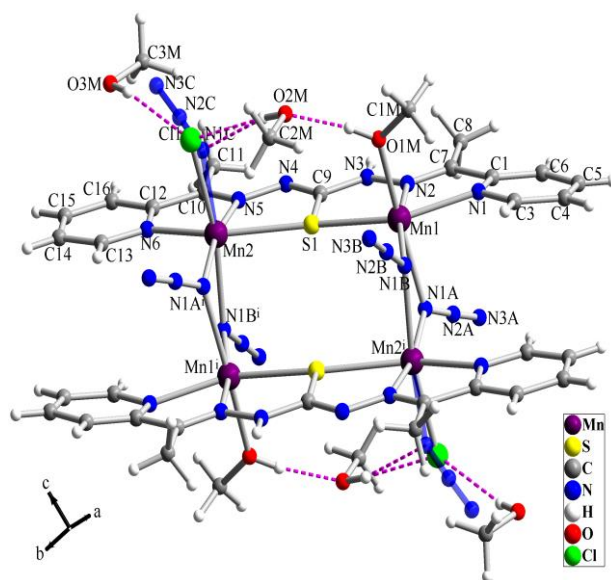


Figure 4. Molecular structure of compound **2** with atom numbering scheme (symmetry code: (i) $-x+1, -y+1, -z+1$). Pink dashed lines show hydrogen bond interactions. One of the disordered methanol molecules is omitted for clarity.

The uncoordinated methanol molecule in the crystal structure of **2** is located between two axial positions of the Mn(II) ions and connects the axial ligands by hydrogen bond interactions. The OH group of coordinated methanol molecules creates O–H···O hydrogen bond with oxygen of uncoordinated methanol molecule. The OH group of uncoordinated methanol molecules also form O–H···N or O–H···Cl hydrogen bond with the axial position of next Mn(II) ion. Moreover, the NH and CH groups are involved in formation of intermolecular hydrogen bond interactions with the nitrogen atom of the bridging azide groups of the neighboring molecules to create a 1D polymeric chain along the crystallographic *a* axis (see Figure 5 and Table 3). Moreover, there are some other weak C–H···Cl, C–H···N and C–H···O hydrogen bonds in the crystal of **2** which contribute in stabilization of the structure.

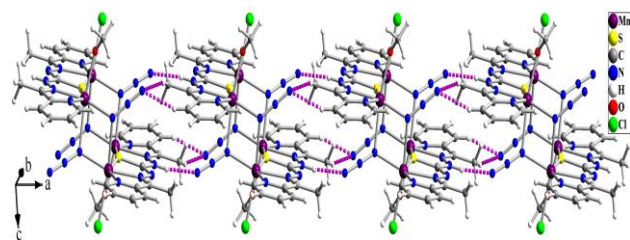


Figure 5. 1D polymeric chain obtained by intermolecular hydrogen bond interactions (shown as dashed pink lines) in the crystal structure of compound **1**. Uncoordinated methanol molecules are omitted for clarity.

Comparison of the structure of **1** and **2** indicates the nature of pseudo-halide ligand (N_3^- and SCN^-) has considerable influence on the structure and nuclearity of the final product and also coordination mode of the thiocarbohydrazone ligand. Compound **2** is a tetranuclear cluster and the ligand is coordinated to the metal ions as mono-negative involving all of its suitable donor atoms while in compound **1** the ligand is coordinated as neutral ligand and part of its donor atoms are not coordinated to the metal ion. The higher coordination and bridging ability of azide ligand in comparison to SCN^- is one of the effective parameters in this observation. This matter is also previously observed in preparing Mn(II) coordination compounds with azide and thiocyanate with Schiff base ligands.³⁷ Moreover, the basic character of sodium azide is also the next parameter that changes the coordination mode of the ligand by effecting on the formation of mono-negative ligand. The effect of sodium azide in the coordination mode of hydrazone ligands is also previously reported.³⁸ It should be noted that in compound **2** the coordination and bridging ability of central sulfur atom was increased by elimination of the NH proton and formation of thiolate group ($C-S^-$) which provides higher electron density on the S atom. In compound **1** the sulfur atom has low ability to act as bridging atom by considering its

neutral character ($C=S$) and low electron density for donating to metal ions.

4. CONCLUSIONS

In summary, two new Mn(II) coordination compounds were synthesized by the reaction of $MnCl_2 \cdot 4H_2O$ with thiocarbohydrazone ligand and $KSCN$ or NaN_3 in methanol. The compounds were characterized by spectroscopic methods and single crystal X-ray analysis. Compound **1** is a mononuclear Mn(II) coordination compound while **2** is an azido bridged tetranuclear Mn(II) cluster. Thiocarbohydrazone ligand is coordinated to Mn(II) ion as a neutral tridentate N_2S -donor ligand. In compound **2** the ligand is coordinated to Mn(II) ions as a mononegative N_4S -donor ligand. In **2**, the azide anions together with sulfur atom of thiocarbohydrazone ligand act as bridging ligand and connect four Mn(II) ions to each other. The FT-IR spectra of **1** and **2** show the characteristic bands of SCN^- and N_3^- anions, respectively. The results indicated that the pseudo-halide SCN^- and N_3^- anions have considerable effect on the structure and nuclearity of the coordination compounds.

CONFLICTS OF INTEREST

There is no conflict of interest to declare.

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Supplementary data

CCDC 2125683 and 2125684 contain the supplementary crystallographic data for **1** and **2**, respectively which can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

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