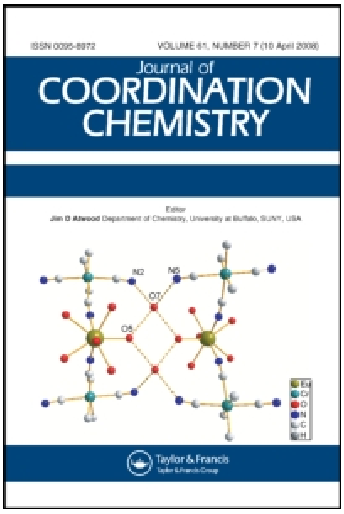

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Synthesis and characterization of polymeric Ni(II) complexes of 4-(4-aminobenzyl)benzenamine (abba) and 4-(4-aminophenylthio)benzenamine (aptba) with thiocyanate

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Two one-dimensional complexes, $[Ni(SCN)_2(abba)_2]_n$ (abba = 4-(4-aminobenzyl)benzenamine) (**1**) and $[Ni(SCN)_2(aptba)_2]_n$ (aptba = 4-(4-aminophenylthio)benzenamine) (**2**), were synthesized and characterized by EA, IR, X-ray crystallography and thermal analysis. The single crystal X-ray structural analyses of **1** and **2** show the complexes to be 1D chain polymers as a result of dibenzenamine (dba) bridging. Each Ni is six-coordinate and adopts a slightly distorted octahedral geometry with four N atoms from four dba ligands and two N atoms from two NCS-groups. Adjacent Ni atoms and two dba ligands form a 24-membered macrocycle. Thermogravimetric analysis and differential thermogravimetric analysis of **2** show that the thermal decomposition of **2** includes four transitions.

Keywords: Self-assembled nickel polymer; Crystal structure; Thermal chemical properties

1. Introduction

Design and construction of solid state coordination polymers by molecular self-assembly, is currently the most efficient approach towards the design of one-, two-, and three-dimensional network materials of potential utility in fields such as catalysis [1–3], nonlinear optics [4], molecular magnetic materials [5], electrical conductivity [6] and molecular recognition [7]. The use of bridging ligands in combination with metal ions and SCN radicals has attracted much interest [8–11]. It is known that 4,4′-bipyridine and dithioethers are good bridging ligands, extensively used in synthesis of framework structures [12–15]. With the purpose of extending relevant structural types and establishing proper synthetic strategies leading to the desired species, we succeeded in synthesizing the coordination polymers $[Ni(SCN)_2(abba)_2]_n$ [abba = 4-(4-aminobenzyl)-benzenamine] (**1**) and $[Ni(SCN)_2(aptba)_2]_n$ [aptba = 4-(4-aminophenylthio)benzenamine] (**2**). In this article, we report the syntheses and characterization of the 1D polymers.

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2. Experimental

2.1. *Apparatus*

All chemicals were of analytical reagent grade and used without further purification. Infrared spectra were taken on a Nicolet 510P FT-IR spectrometer (KBr). Elemental analyses were performed on a Perkin–Elmer 240 analyzer. The thermogravimetric analyses (TGA) were performed with a NETZSCH TG209 thermal analyzer.

2.2. *Preparation of the complexes*

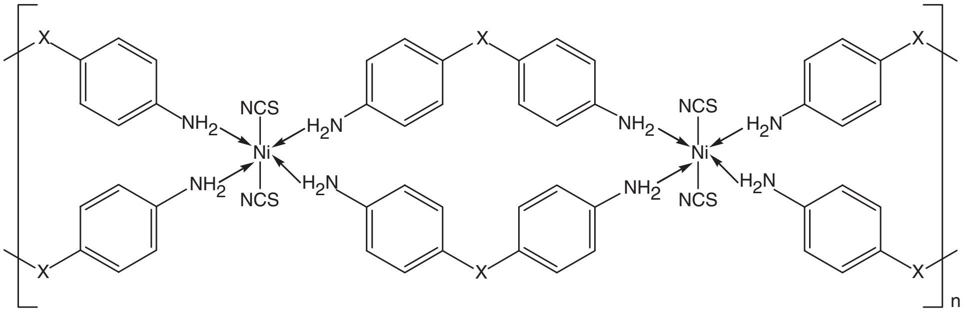
To a hot solution of the corresponding dibenzenamine (1.02 mmol) in ethanol (10 mL), was added slowly $Ni(NO_3)_2 \cdot 6H_2O$ (0.29 g, 1.06 mmol) and NH_4SCN (0.15 g, 2.03 mmol) in hot ethanol (10 mL). After vigorous stirring, the pH value of the resulting solution was adjusted to 5.0 by addition of dilute HNO_3. The mixture was then allowed to evaporate at room temperature. Green crystals suitable for X-ray diffraction were deposited in one week.

For complex **1**, 60% yield. Anal. Calcd for $C_{28}H_{28}NiN_6S_2$: C, 58.86, H, 4.94, N, 14.71%; Found: C, 58.23, H, 5.18, N, 14.83%. IR data (cm^{-1}): 3326m, 3255m, 3158w, 2096vs, 1614m, 1586w, 1441s, 1247w, 1236w, 1044s, 1010s, 827w, 808m, 770w, 593w, 579w, 523w.

For complex **2**, yield: 67%. Anal. Calcd for $C_{26}H_{24}NiN_6S_4$: C, 51.43, H, 3.96, N, 13.85%; Found: C 51.88, H 3.75, N 13.98%. IR data (cm^{-1}): 3304m, 3145w, 3062w, 2115vs, 1601m, 1493s, 1422w, 1238w, 1054s, 1031s, 934w, 818m, 708w, 637w, 598w, 528w. The preparative scheme of the title complexes is shown in Scheme 1.

2.3. *Crystallographic studies*

Suitable crystals of the title complexes were mounted on a BRUKER SMART 1000 CCD diffractometer. Reflection data were measured at 20°C using Mo-Kα radiation ($\lambda = 0.71073$ Å) with a graphite monochromator. The technique used was ω-scan. Empirical absorption corrections were carried out by using the SADABS [16] program. The structures were solved by direct methods and refined by least squares on F^2 using



1: X = C; **2**: X = S

Scheme 1. The formula of the title complexes.

Table 1. Crystal data and structure refinement parameters for the title complexes.

	Complex **1**	Complex **2**
Formula	$C_{28}H_{28}N_6NiS_2$	$C_{26}H_{24}N_6NiS_4$
Formula weight	571.39	607.48
Colour	Green	Green
Crystal system	Monoclinic	Monoclinic
Space group	$P21/c$	$C2/m$
a (Å)	11.720(6)	11.2892(17)
b (Å)	9.400(5)	16.663(2)
c (Å)	12.634(6)	7.4223(11)
β (°)	104.654(9)	108.926(2)
V (Å^3)	1346.6(12)	1320.7(3)
Z	2	2
$D_{(\mathrm{Calcd})}$ (g cm^{-3})	1.409	1.528
F(000)	596	628
Crystal size (mm^3)	0.26 × 0.31 × 0.53	0.09 × 0.20 × 0.37
Temperature (K)	293	293
θ ranges (°)	1.8, 27.1	2.3, 26.0
Reflections collected	2899	1350
Independent reflections	2445	1248
Final R indices [$I > 2\sigma(I)$]	0.0304	0.0251

Table 2. Selected bond distances (Å) and angles (°).

Complex **1**		Complex **2**	
Ni1–N1	2.165(2)	Ni–N1	2.188(1)
Ni1–N3	2.012(2)	Ni–N2	2.028(2)
S1–C14	1.618(2)	S1–C6	1.775(2)
N1–C1	1.431(3)	S2–C7	1.644(2)
N2–C11	1.434(3)	N1–C3	1.440(2)
N3–C14	1.146(3)	N2–C7	1.149(3)
N1–Ni1–N3	92.22(8)	N1–Ni1–N2	86.95(5)
N1–Ni1–N2A	85.45(7)	N1–Ni1–N2B	93.05(5)
N1–Ni1–N1C	180.00	N1–Ni1–N1D	90.86(5)
N1–Ni1–N3C	87.78(8)	N2–Ni1–N2B	180.00
N1–Ni1–N2D	94.55(7)	N1–Ni1–N1B	89.14(5)
N2A–Ni1–N3	87.03(7)	N1–Ni1–N1C	180.00
N2D–Ni1–N3	92.97(7)	N1B–Ni1–N2	93.05(5)
N1C–Ni1–N3C	92.22(8)	S2–C7–N2	178.9(2)
S1–C14–N3	178.4(2)		

Table 3. Hydrogen-bonding geometry (Å, °).

Complexes	D–H···A	D–H	H···A	D···A	D–H···A
1	N1–H1B···S1$^{\mathrm{i}}$	0.85(3)	2.56(3)	3.384(3)	162(2)
2	N1–H1A···S1$^{\mathrm{ii}}$	0.90	2.82	3.573(1)	141
	N1–H1C···S2$^{\mathrm{iii}}$	0.90	2.65	3.552(2)	177

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

the SHELXTL [17] software package. All non-H atoms were anisotropically refined; hydrogen atoms were located by difference synthesis and refined isotropically. The molecular graphics were plotted using SHELXTL [17]. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-Ray Crystallography [18].

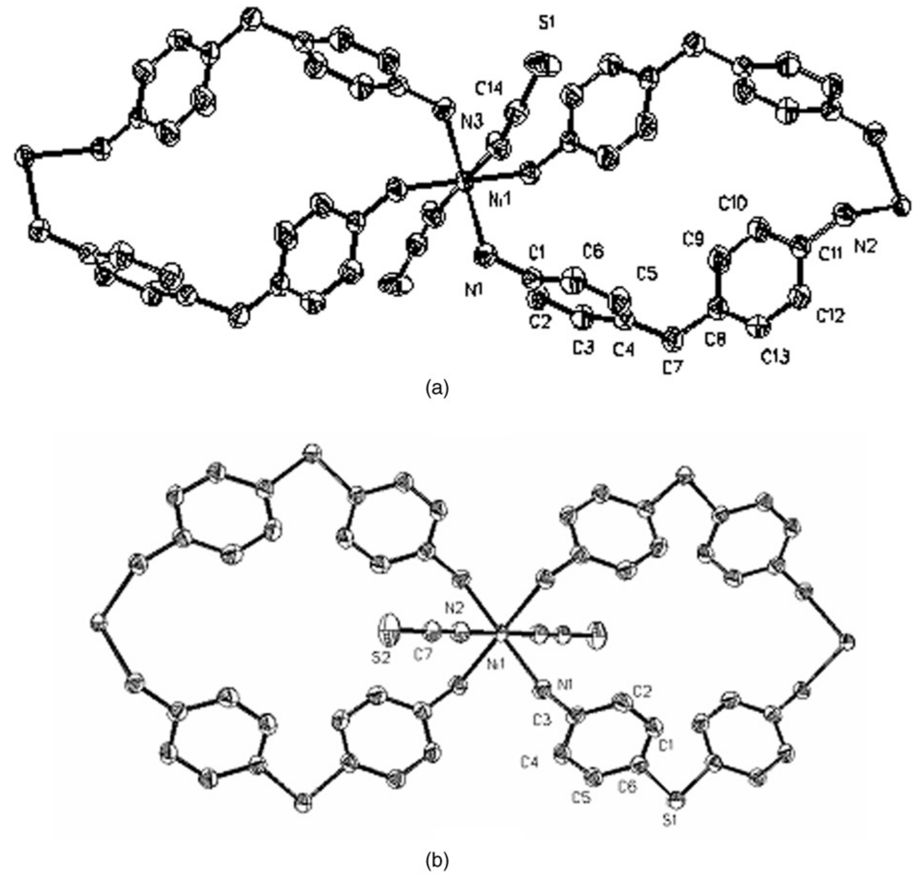


Figure 1. ORTEP diagrams of 1 (a) and 2 (b) with the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

3. Results and discussion

3.1. *X-ray crystal structure of the title compounds*

The final atomic parameters and equivalent isotropic thermal parameters for the non-hydrogen atoms of the two complexes are given in table 1. Selected bond lengths and angles are illustrated in table 2. The hydrogen bonding geometries are shown in table 3. ORTEP drawings of the title complexes are shown in figure 1 and figure 2 represents a perspective view of the crystal packing in the unit cell for the complexes. **1** and **2** belong to the same monoclinic crystal system, but differ in space groups, $P2_1/c$ for **1** and $C2/m$ for **2**. All bond lengths and angles in **1** and **2** are comparable.

The crystal structures of both **1** and **2** consist of one-dimensional polymeric units with the basic repeating dimeric [Ni(SCN)$_2$(Abba)$_2$] and [Ni(SCN)$_2$(Aptba)$_2$], respectively. For **1** and **2**, each Ni is six-coordinate in a slightly distorted octahedron with equatorial positions occupied by four bibenzenamine ligands [Ni–N1 2.165(2) Å for **1**, Ni–N1 2.188(1) Å for **2**] and the axial sites are occupied by two N atoms NCS groups [Ni–N3 2.012(2) Å for **1**, Ni–N2 2.028(2) Å for **2**].

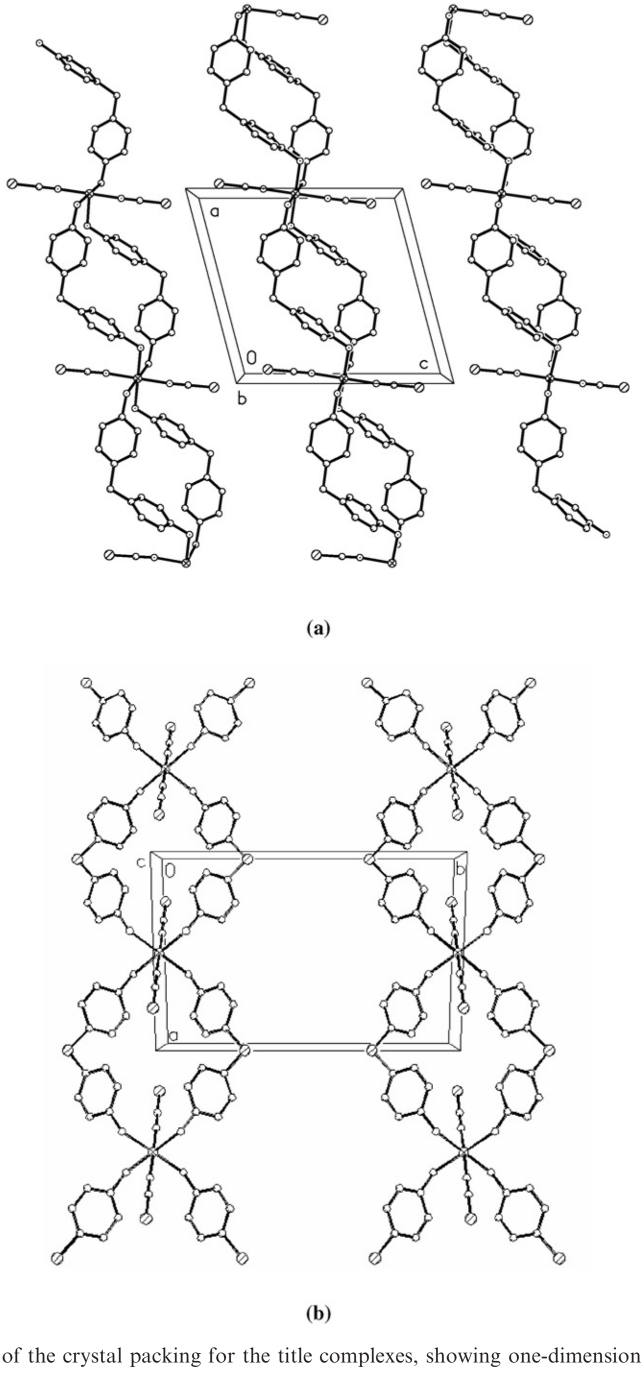


Figure 2. A view of the crystal packing for the title complexes, showing one-dimensional chain polymers.

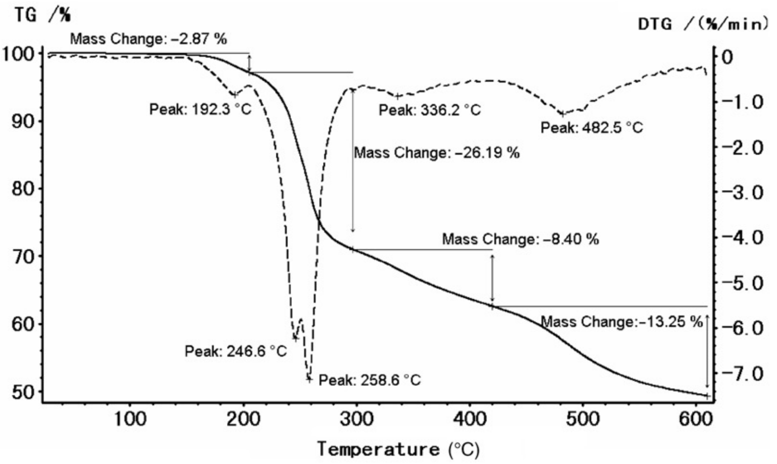


Figure 3. Thermal analysis curves of complex **2**.

In each complex, the dba ligands are μ^2-bridges connecting Ni atoms into chains along the a axis, with the repeating unit: –Ni–(dba)$_2$–Ni–(dba)$_2$–. Adjacent Ni atoms and two dba ligands form a 24-membered ring, in which the neighboring distances of two Ni atoms are 11.720(6) Å for **1** and 11.322(14) Å for **2**, while that for the two C7 atoms is 8.023(1) Å for **1** and 9.699(1) Å for two S atoms in **2**, respectively. Individual polymeric chains are almost parallel to each other and adjacent chains are linked into two-dimensional layers by N1–H1A···S1 hydrogen bonds. In **2**, the N1–H1C···S2 hydrogen bonds, however, connect the layers into a three-dimensional framework. The packing is further stabilized by $\pi\cdots\pi$ interactions between the benzene rings with a Cg···Cg distance of 3.691 Å [Cg denotes the centroids of the benzene ring; symmetry code: $1/2-x$, $1/2-y$, $1-z$].

3.2. *IR spectra*

The IR spectra exhibit strong characteristic asymmetric absorption bands at 2095 and 2115 cm^{-1} for **1** and **2**, respectively, resulting from SCN. The IR spectra of the title complexes show bands (3326 and 3158 cm^{-1} for **1**, 3304 and 3145 cm^{-1} for **2**) due to N–H stretching. In complex **2**, the strong bands at 1054 and 1031 cm^{-1} are assigned as the sulfoether group. The IR spectroscopic studies show agreement with the X-ray crystal structure analysis of the complexes.

3.3. *Thermal analysis*

Thermal analysis curves of the title compound are shown in figure 3. Thermogravimetric (TG) analysis and differential thermogravimetric (DTG) analysis show that the thermal decomposition of the title compound includes four transitions, all corresponding to exothermal processes. A peak at 192.3°C corresponds to removal of one SCN^- anion. The second weight loss (26.19%) occurs between 200 and 300°C (strong endothermal peak observed at 246.6 and 258.6°C in DTA), corresponding to the loss of two SCN^- anions. A weak peak at 336.2°C implying the loss of two –NH_2 groups and endothermal peak is observed at 482.5°C suggesting the decomposition of **2**.

Supplementary material

Crystallographic data for the title two complexes reported in this article has been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 624118 and 623287. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union road, Cambridge CB21EZ, UK (Fax: + 44-1223-336-033; Email: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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