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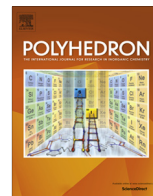


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# Synthesis and characterization of five new thiocyanato- and cyanato-metal(II) complexes with 4-azidopyridine as co-ligand

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## ABSTRACT

Five new metal(II) pseudohalide complexes with 4-azidopyridine (4-azpy) have been synthesized,  $[\text{Ni}_2(4\text{-azpy})_6(\text{NCS})_4]$  (**1**),  $[\text{Co}(4\text{-azpy})_4(\text{NCS})_2]$  (**2**),  $[\text{Mn}(4\text{-azpy})_4(\text{NCS})_2]$  (**3**),  $[\text{Ni}(4\text{-azpy})_4(\text{NCO})_2]$  (**4**), and  $[\text{Co}(4\text{-azpy})_2(\text{NCO})_2]$  (**5**), and characterized by IR, UV–Vis spectroscopy and single crystal X-ray diffraction. The crystal structure of the dimeric complex **1** features terminal and  $\mu(\text{N,S})$ -bridging thiocyanates, and 4-azidopyridine ligands in *mer*-conformation around the distorted Ni(II) octahedra. The monomeric complexes **2–4** form distorted octahedral  $\text{MN}_6$  geometries with two N-coordinated terminal pseudohalides in *trans*-arrangement. The  $\text{CoN}_4$  tetrahedron in **5** is formed by two cyanate anions and two 4-azidopyridine molecules. The magnetic properties of the dimeric complex **1** are reported.

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## 1. Introduction

Small linear triatomic pseudo halide ions  $\text{N}_3^-$ ,  $\text{NCS}^-$ ,  $\text{NCO}^-$  and  $\text{NCSe}^-$  have been used in the design and self-assembly of coordination polynuclear and polymeric compounds. These ions have the capability of bridging metal centers simultaneously leading to the construction of different framework and interesting topology [1–37] where extensive amount of literature and many compounds of different coordination binding modes have been reported with the azide ligand,  $\text{N}_3^-$  [1–3]. On the other hand, less effort have been directed to the  $\text{NCX}^-$  ligands ( $\text{X} = \text{S}, \text{O}$  or  $\text{Se}$ ), probably because of the fact that the azide ion is a better ligand in propagating the magnetic coupling between the paramagnetic metal centers compared to the thiocyanate,  $\text{NCS}^-$  or the cyanate ion,  $\text{NCO}^-$  ligands. In addition to the ambidentate nature of the last two ions which may lead to different linkage isomeric species, the softness or hardness of the terminal atom X may play another role for the preference of the metal ion to bind these ligands through the N- or the X-terminal of the ligands (S-atom in  $\text{NCS}^-$  or O-atom in  $\text{NCO}^-$ ). The N-side in  $\text{NCS}^-$  or  $\text{NCO}^-$  is at the borderline between of hard/

soft Lewis base and hence it can bind any metal ion, whereas S-soft side in  $\text{NCS}^-$  is associated with soft metal ion and the corresponding hard O-side in  $\text{NCO}^-$  has more preference to hard metal ion. However, the preference to the coordination bonding side may change depending on the nature of coordinated ancillary Co-ligand(s) as well as the steric environment imposed by these ligands.

Focusing our attention here on the thiocyanate and cyanate complexes, several coordination bonding modes have been reported on these ligands which range from single monodentate [4,5] to multi-bonding modes. In case of the bridging thiocyanate complexes the bonding modes  $\mu_{1,3}\text{-NCS}^-$  (**I**) [6–20],  $\mu_{1,1}\text{-NCS}^-$  (**II**) [21,22a],  $\mu_{3,3}\text{-NCS}^-$  (**III**) [21a,22],  $\mu_{1,1,3}\text{-NCS}^-$  (**IV**) [23],  $\mu_{1,3,3}\text{-NCS}^-$  (**V**) [24] and  $\mu_{1,3,3,3}\text{-NCS}^-$  (**VI**) [25] have been reported. Limited number of bonding modes have been observed with the bridging cyanate ligand:  $\mu_{1,3}\text{-NCO}^-$  (**VII**) [26,27],  $\mu_{1,1}\text{-NCO}^-$  (**VIII**) [27–37],  $\mu_{3,3}\text{-NCO}^-$  (**IX**) [37] and  $\mu_{1,1,1,1}\text{-NCO}^-$  (**X**) [38]. These bridging bonding modes are illustrated in Chart 1. However, we should emphasize that bonding modes summarized in this chart may not be the only existing modes but other modes may be found. Most of these coordination modes generate metal complexes of interesting and fascinating structures with different topologies and dimensionality (1D, 2D and 3D) [7c,9–14,16,22a]. In general, like the azide bridging the  $\mu_{1,3}\text{-NCX}^-$  bridging modes tend to

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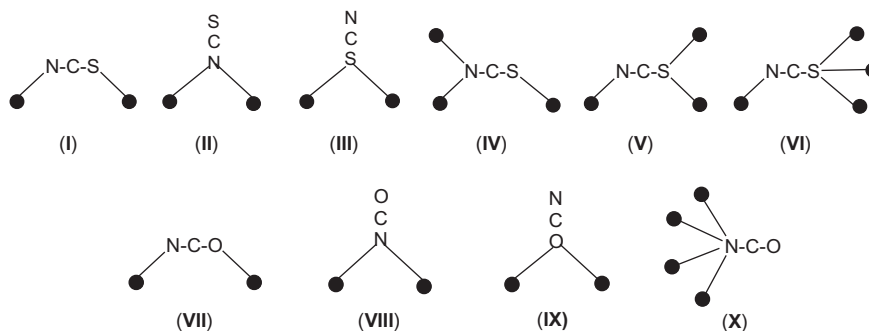


Chart 1. Some thiocyanate and cyanate coordination bridging modes.

exhibit antiferromagnetic exchange interactions (AF), whereas the corresponding  $\mu_{1,1}$ -NCX<sup>−</sup> or  $\mu_{3,3}$ -NCX<sup>−</sup> bonding mediates weak to moderate ferromagnetic coupling (FM) [7,9–11,15,16,21c,27].

In an effort to explore the coordination bonding modes of the thiocyanate and cyanate ligands with divalent metal ions (Mn<sup>2+</sup>, Co<sup>2+</sup> and Ni<sup>2+</sup>) and how the metal ion might affect the bonding mode of NCX<sup>−</sup> and the geometry of the resulting compounds, we report here the synthesis and structural characterization of some thiocyanato- and cyanato-metal(II) complexes using 4-azidopyridine (4-azpy) as a coligand as well as the magnetic properties of the dinuclear doubly bridged thiocyanato complex **1**.

## 2. Experimental

### 2.1. Materials and physical measurements

The preparation of 4-azidopyridine was performed according to literature [39]. All other materials used in this study were reagent grade quality. Infrared spectra of solid complexes were recorded on a Bruker Alpha P (platinum-ATR-cap). UV–Vis(NIR) spectra were performed with a LS950 Perkin-Elmer Lambda-spectrometer in the range from 4000–45000 cm<sup>−1</sup> (pulsed D<sub>2</sub>O lamp). Elemental microanalyses were carried out with an Elementary Vario EN 3 analyzer.

**Caution:** Azide compounds are potentially explosive and should be handled with great care and in small quant.

### 2.2. Synthesis

#### 2.2.1. Preparation of [Ni<sub>2</sub>(4-azpy)<sub>6</sub>(NCS)<sub>4</sub>] (**1**)

A mixture of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.237 g, 1.0 mmol), 4-azidopyridine (0.240 g, 2.0 mmol) and solid KSCN (0.486 g, 5 mmol) were dissolved in 10 mL of dist. H<sub>2</sub>O with stirring and heating to 85 °C for 20 min and afterwards filtered. The resulting blue-green solution was placed in a compartment dryer (50 °C) over night. Afterwards the solution was slowly cooled to room temperature. Long green needles of **1** were separated after two days. Yield: 0.178 g, 50%. *Anal.* Calc. for C<sub>34</sub>H<sub>24</sub>N<sub>28</sub>Ni<sub>2</sub>S<sub>4</sub> (1070.47 g/mol): C, 38.2; H, 2.3; N, 36.6. Found: C, 38.5; H, 2.4; N, 36.4%. Selected IR bands (cm<sup>−1</sup>): 2418 (w), 2365 (w), 2344 (w), 2266 (m), 2131 (s,sh), 2103 (vs), 2078 (vs); 1635 (m), 1600 (s), 1558 (s), 1500 (s), 1427 (m), 1293 (s), 1208 (s), 1132 (m), 1012 (m), 811 (s), 785 (m), 729 (w), 676 (s), 622 (m), 520 (m), 475 (m), 461 (m), (s = strong, m = medium, w = weak, sh = shoulder, v = very).

#### 2.2.2. Preparation of [Co(4-azpy)<sub>4</sub>(NCS)<sub>2</sub>] (**2**)

A mixture of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.236 g, 1.0 mmol), 4-azidopyridine (0.240 g, 2.0 mmol) and solid KSCN (0.486 g, 5.0 mmol) were dissolved in 15 mL of dist. H<sub>2</sub>O with stirring and heating to 80 °C for 45 min. The hot purple solution was filtered and placed in a compartment dryer (50 °C) over night. Following two days at room

temperature dark purple crystals of **2** began to grow. Yield: 0.213 g, 65%. *Anal.* Calc. for C<sub>22</sub>H<sub>16</sub>CoN<sub>18</sub>S<sub>2</sub> (655.60 g/mol): C, 40.3; H, 2.5; N, 38.5. Found: C, 40.0; H, 2.4; N, 38.2%. Selected IR bands (cm<sup>−1</sup>): 2436 (w), 2415 (w), 2280 (w), 2266 (s), 2205 (w), 2146 (m,sh), 2131 (vs,sh); 2106 (vs), 2063 (vs), 1631 (m), 1589 (s), 1560 (s), 1497 (s), 1423 (m), 1356 (s), 1313 (s), 1295 (s), 1285 (s), 1239 (s), 1215 (s), 1137 (s), 1108 (m), 1059 (m), 1005 (s), 974 (w), 955 (w), 863 (w), 832 (m), 818 (s), 729 (s), 676 (s), 530 (m), 516 (m), 474 (m).

#### 2.2.3. Preparation of [Mn(4-azpy)<sub>4</sub>(NCS)<sub>2</sub>] (**3**)

A mixture of MnCl<sub>2</sub>·2H<sub>2</sub>O (0.161 g, 1.0 mmol), 4-azidopyridine (0.240 g, 2.0 mmol) and solid KSCN (0.486 g, 5.0 mmol) were dissolved in 10 mL of dist. H<sub>2</sub>O with stirring and heating to 50 °C for 30 min. The hot solution was filtered and placed in a compartment dryer (50 °C) for one day. Afterwards the solution was slowly cooled to room temperature to produce colourless crystals of **3** which were separated after two days. Yield: 0.228 g, 70%. *Anal.* Calc. for C<sub>22</sub>H<sub>16</sub>MnN<sub>18</sub>S<sub>2</sub> (651.59 g/mol): C, 40.6; H, 2.5; N, 38.7%. Found: C, 40.3; H, 2.6; N, 39.0. Selected IR bands (cm<sup>−1</sup>): 2432 (w), 2280 (w), 2262 (w), 2153 (m,sh), 2131 (vs,sh); 2106 (vs), 2053 (vs), 1632 (m), 1593 (s), 1562 (s), 1498 (s), 1427 (m), 1356 (s), 1335 (w), 1314 (s), 1295 (s), 1285 (s), 1243 (s), 1215 (s), 1132 (s), 1104 (m), 1059 (m), 1026 (w), 1005 (s), 974 (w), 955 (w), 863 (w), 832 (m), 818 (s), 729 (s), 676 (s), 534 (m), 517 (m), 475 (m).

#### 2.2.4. Preparation of [Ni(4-azpy)<sub>4</sub>(NCO)<sub>2</sub>] (**4**)

A mixture of NiCl<sub>2</sub>·6H<sub>2</sub>O (0.237 g, 1.0 mmol), 4-azidopyridine (0.240 g, 2.0 mmol) and solid KOCN (0.406 g, 5 mmol) were dissolved in 10 mL of dist. H<sub>2</sub>O with stirring and heating to 85 °C for 20 min and afterwards filtered. The resulting green solution was placed in a compartment dryer (50 °C) over night. Afterwards the solution was slowly cooled to 4 °C. Green needles of **4** were separated after three days. Yield: 0.203 g, 65%. *Anal.* Calc. for C<sub>22</sub>H<sub>16</sub>Ni<sub>18</sub>NiO<sub>2</sub> (623.22 g/mol): C, 42.4; H, 2.6; N, 40.5. Found: C, 42.1; H, 2.5; N, 40.2%. Selected IR bands (cm<sup>−1</sup>): 2425 (w), 2358 (w), 2266 (m), 2226 (s), 2184 (vs), 2132 (vs); 2103 (vs), 2068 (vs), 1635 (m), 1601 (s), 1565 (s), 1503 (s), 1427 (m), 1356 (w), 1335 (w), 1318 (m), 1295 (s), 1242 (m), 1212 (s), 1134 (m), 1064 (m), 1018 (s), 817 (s), 728 (m), 679 (s), 666 (s), 620 (s), 598 (m), 536 (m), 517 (s), 482 (w).

#### 2.2.5. Preparation of [Co(4-azpy)<sub>2</sub>(NCO)<sub>2</sub>] (**5**)

A mixture of CoCl<sub>2</sub>·6H<sub>2</sub>O (0.237 g, 1.0 mmol), 4-azidopyridine (0.301 g, 2.5 mmol) and solid KOCN (0.406 g, 5.0 mmol) were dissolved in 10 mL of dist. H<sub>2</sub>O with stirring and heating to 50 °C for 25 min. The hot purple solution was filtered and placed in a compartment dryer (50 °C) over night. Following one day at room temperature blue crystals of **5** began to grow. Yield: 0.260 g, 68%. *Anal.* Calc. for C<sub>12</sub>H<sub>8</sub>CoN<sub>10</sub>O<sub>2</sub> (383.21 g/mol): C, 37.6; H, 2.1; N, 36.6. Found: C, 37.3; H, 2.0; N, 36.9%. Selected IR bands (cm<sup>−1</sup>): 2425

(w), 2344 (w), 2268 (m), 2226 (vs), 2198 (vs), 2139 (vs), 2110 (vs), 2078 (vs), 1637 (w), 1605 (s), 1558 (s), 1494 (s), 1476 (m), 1433 (m), 1354 (m), 1290 (s), 1285 (s), 1247 (m), 1207 (s), 1134 (s), 1057 (w), 1027 (s), 1005 (s), 981 (w), 856 (w), 840 (m), 828 (m), 816 (s) 727 (m), 681 (s), 665 (m), 614 (s), 536 (m) 516 (s), 458 (w).

### 2.3. X-ray crystal structure analysis

The X-ray single-crystal data of compounds **1–5** were collected on a Bruker-AXS APEX CCD diffractometer at 100(2) K. The crystallographic data, conditions retained for the intensity data collection and some features of the structure refinements are listed in Table 1. The intensities were collected with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data processing, Lorentz-polarization and absorption corrections were performed using APEX, and the SHELX computer programs [40]. The structures were solved by direct methods and refined by full-matrix least-squares methods on  $F^2$ , using the SHELXTL [41] program package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps, assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical constraints. Molecular plots were performed with the Mercury [42] program.

### 2.4. Magnetic measurements

Magnetic susceptibility measurements under several magnetic fields in the temperature range 2–300 K and magnetisation measurements in the field range 0–5 T were performed with a Quantum Design MPMS-XL SQUID magnetometer at the Magnetochemistry Service of the University of Barcelona on polycrystalline samples. Pascal's constants were used to estimate the diamagnetic corrections, which were subtracted from the experimental susceptibilities to give the corrected molar magnetic susceptibilities.

## 3. Results and discussion

### 3.1. Spectroscopic characterization of the complexes

The IR spectra of the complexes **1–3** display a series of very strong absorption bands in the 2131–2053  $\text{cm}^{-1}$  region due to

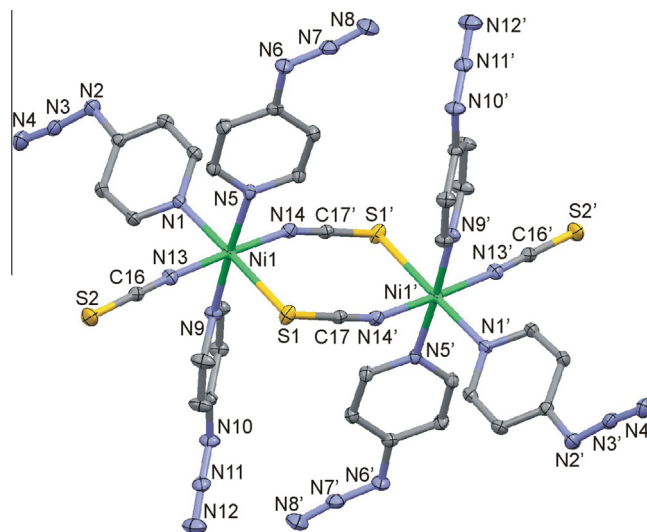


Fig. 1. Perspective view of **1** together with the atom numbering scheme. Symmetry code is according to Table 2.

the asymmetric stretching frequency,  $\nu_{\text{as}}(\text{NCS}^-)$  of the isothiocyanato groups superimposed by  $\nu_{\text{as}}(\text{N}_3^-)$  vibrations of the 4-azidopyridine ligands. The IR spectra of complexes **4** and **5** display the very strong  $\nu_{\text{as}}(\text{NCO}^-)$  of cyanato groups centered around 2200  $\text{cm}^{-1}$  separated from the  $\nu_{\text{as}}(\text{N}_3^-)$  vibrations of the 4-azidopyridine ligands in the 2132–2078  $\text{cm}^{-1}$  region.

The solid UV–Vis–NIR spectra exhibit three absorption bands at 904, 582 and 326 nm for complex **1**, and at 1066, 656 and 396 nm for complex **4**. These bands are assigned to the electronic transitions  ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}$ ,  ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}$  and  ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}$ , respectively for Ni(II) in octahedral environment. Similarly, in complex **2** three absorption bands were observed at 1056, 506 and 344 nm which can be assigned to the allowed transitions  ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ ,  ${}^4\text{T}_{2g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$  and  ${}^4\text{A}_{2g} \leftarrow {}^4\text{T}_{1g}(\text{F})$ , respectively in Co(II) in octahedral environment. The diffuse reflectance spectrum for compound **5** exhibits three transitions attributed to spin-allowed transitions from  ${}^4\text{A}_2(\text{F})$  to  ${}^4\text{T}_2(\text{F})$ , at 1390 nm, to  ${}^4\text{T}_1(\text{F})$  at 1004 nm and to  ${}^4\text{T}_1(\text{P})$  at 586 nm corresponding to high-spin tetrahedral Co(II) [43].

Table 1  
Crystallographic data and processing parameters.

Compound	1	2	3	4	5
Empirical formula	$\text{C}_{34}\text{H}_{24}\text{N}_{28}\text{Ni}_2\text{S}_4$	$\text{C}_{22}\text{H}_{16}\text{CoN}_{18}\text{S}_2$	$\text{C}_{22}\text{H}_{16}\text{MnN}_{18}\text{S}_2$	$\text{C}_{22}\text{H}_{16}\text{Ni}_{18}\text{NiO}_2$	$\text{C}_{12}\text{H}_8\text{CoN}_{10}\text{O}_2$
Formula mass	1070.47	655.60	651.61	623.22	383.21
System	monoclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
$a$ (Å)	8.2019(4)	19.0396(17)	19.1886(7)	10.0060(13)	5.5331(6)
$b$ (Å)	15.6290(7)	7.8896(6)	7.9392(3)	15.870(2)	9.6117(9)
$c$ (Å)	18.0638(8)	20.9844(18)	20.9139(8)	17.819(2)	15.5430(14)
$\alpha$ (°)	90	90	90	87.22(2)	74.56(2)
$\beta$ (°)	101.487(2)	115.904(14)	116.443(2)	78.48(2)	81.08(2)
$\gamma$ (°)	90	90	90	76.98(2)	78.15(2)
$V$ (Å <sup>3</sup> )	2269.17(18)	2835.5(5)	2852.74(19)	2701.3(6)	775.38(16)
$Z$	2	4	4	4	2
$T$ (K)	100(2)	100(2)	100(2)	100(2)	100(2)
$\mu$ (mm <sup>−1</sup> )	1.077	0.803	0.659	0.778	1.139
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.567	1.536	1.517	1.532	1.641
Crystal size (mm)	$0.22 \times 0.16 \times 0.09$	$0.45 \times 0.12 \times 0.08$	$0.31 \times 0.14 \times 0.13$	$0.35 \times 0.15 \times 0.08$	$0.38 \times 0.25 \times 0.08$
$\theta$ max (°)	30.55	25.50	29.62	26.00	26.00
Data collected	106090	20514	152865	20815	5907
Unique reflection/ $R_{\text{int}}$	6949/0.0361	5269/0.0772	8011/0.0402	10468/0.0513	2998/0.0447
Parameters/Restraints	307/0	391/0	391/0	775/0	226/0
Goodness-of-fit (GOF) on $F^2$	1.013	1.297	1.044	1.118	1.285
$R_1/wR_2$ (all data)	0.0236/0.0658	0.0932/0.1805	0.0289/0.0744	0.0668/0.1517	0.0972/0.2091
Residual extrema (e/Å <sup>3</sup> )	0.46/−0.35	0.96/−1.01	0.48/−0.47	0.85/−0.43	1.38/−1.29

**Table 2**Selected bond lengths (Å) and angles (°) for compound **1**.

Ni(1)–N(1)	2.0993(9)	Ni(1)–N(13)	2.0369(10)
Ni(1)–N(5)	2.1037(9)	Ni(1)–N(14)	2.0431(9)
Ni(1)–N(9)	2.1163(9)	Ni(1)–S(1)	2.5481(3)
S(1)–C(17)	1.6441(11)	S(2)–C(16)	1.6340(11)
N(14)–C(17')	1.1589(15)	N(13)–C(16)	1.1639(15)
N(13)–Ni(1)–N(14)	177.66(4)	N(1)–Ni(1)–S(1)	178.29(3)
N(5)–Ni(1)–N(9)	176.68(4)	N(14)–Ni(1)–S(1)	92.13(3)
N(14')–C(17)–S(1)	179.46(10)	N(13)–C(16)–S(2)	179.38(11)
Ni(1)–N(14)–C(17')	162.52(9)	Ni(1)–S(1)–C(17)	101.29(4)
Ni(1)–N(13)–C(16)	176.38(9)		

Symmetry code: (') 1 – x, 2 – y, 1 – z.

### 3.2. Description of the crystal structures

#### 3.2.1. $[\text{Ni}_2(4\text{-azpy})_6(\text{NCS})_4]$ (**1**)

A perspective view of **1**, together with the atom numbering scheme is given in Fig. 1, and selected bond lengths and bond angles are summarized in Table 2. The crystal structure of **1** con-

sists of centrosymmetric neutral dinuclear Ni(II) complexes. Ni(1) is six-coordinated by three pyridine N donor atoms of 4-azidopyridine molecules in a meridional conformation, N(13) of a terminal thiocyanate anion, and N(14) and S(1) of two centrosymmetric related  $\mu_{\text{N,S}}$ -bridging thiocyanato anions, which connect the two metal centers. The  $\text{NiN}_5\text{S}$  chromophore may be described as distorted octahedron with Ni(1)–N bond distances in the range from 2.0369(10) to 2.1163(9) Å and Ni(1)–S(1) bond distance of 2.5481(3) Å. The bond parameters of the di- $\mu_{\text{N,S}}$ -thiocyanato bridges are: N(14)–Ni(1)–S(1) = 92.13(3), Ni(1)–N(14)–C(17') = 162.52(9), Ni(1)–S(1)–C(17) = 101.29(4), N(14)–C(17')–S(1') = 179.46(10)°; N(14)–C(17') = 1.1589(15), S(1)–C(17) = 1.6441(11) Å. The Ni(1)–S(1)···N(14')–Ni(1') torsion angle is 42.2° [('): 1 – x, 2 – y, 1 – z]. The eight-membered  $\text{Ni}_2(\text{NCS})_2$  ring forms a “chair”-like arrangement with acute interplanar angle of 13.0° [i.e.: angle between plane Ni(1)–N(14)–S(1) and plane of the di- $\mu_{\text{N,S}}$ -thiocyanato bridges]. The Ni(1)···Ni(1') intra-dimer distance is 5.6392(4) Å, whereas the shortest inter-dimer metal–metal separation is 8.62019(5) Å. The bond parameters of the terminal N-coordinated  $\text{NCS}^-$  anions are: Ni(1)–N(13)–C(16) = 176.38(9),

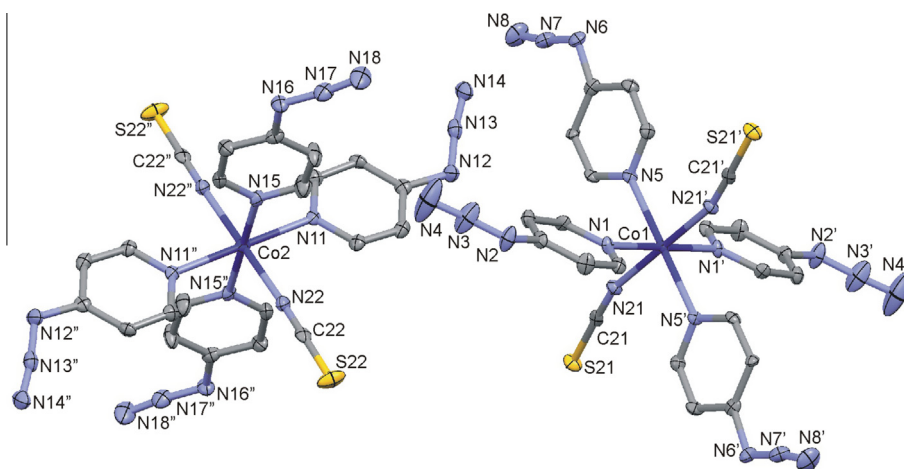


Fig. 2. Perspective view of **2** together with the atom numbering scheme. Symmetry code is according to Table 3.

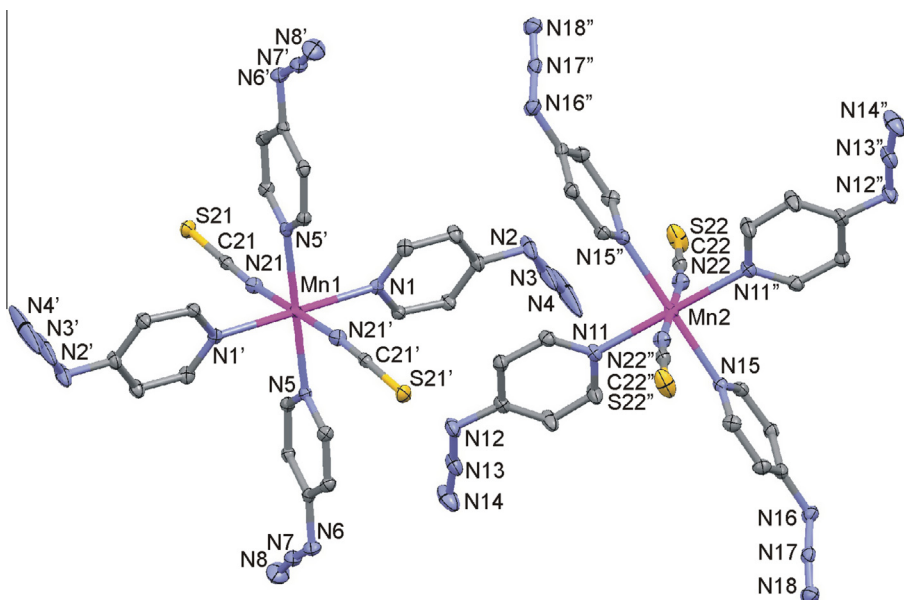


Fig. 3. Perspective view of **3** together with the atom numbering scheme. Symmetry code is according to Table 4.



**Table 3**  
Selected bond lengths (Å) and angles (°) for compound **2**.

Co(1)–N(1)	2.199(4)	Co(2)–N(11)	2.233(5)
Co(1)–N(5)	2.211(4)	Co(2)–N(15)	2.200(5)
Co(1)–N(21)	2.079(5)	Co(2)–N(22)	2.071(5)
N(21)–C(21)	1.168(7)	C(21)–S(21)	1.639(6)
N(22)–C(22)	1.158(7)	C(22)–S(22)	1.639(6)
N(21)–Co(1)–N(21')	180	N(22)–Co(2)–N(22'')	180
Co(1)–N(21)–C(21)	164.1(4)	Co(2)–N(22)–C(22)	173.0(5)
N(21)–C(21)–S(21)	178.1(5)	N(22)–C(22)–S(22)	179.6(4)

Symmetry codes: (') 1 – x, 1 – y, –z; (") 2 – x, –y, 1 – z.

**Table 4**  
Selected bond lengths (Å) and angles (°) for compound **3**.

Mn(1)–N(1)	2.3071(10)	Mn(2)–N(11)	2.3130(11)
Mn(1)–N(5)	2.3058(11)	Mn(2)–N(15)	2.3162(11)
Mn(1)–N(21)	2.1793(11)	Mn(2)–N(22)	2.1690(12)
N(21)–C(21)	1.1651(17)	C(21)–S(21)	1.6324(13)
N(22)–C(22)	1.1596(18)	C(22)–S(22)	1.6261(14)
N(21)–Mn(1)–N(21')	180	N(22)–Mn(2)–N(22'')	180
Mn(1)–N(21)–C(21)	162.82(10)	Mn(2)–N(22)–C(22)	171.73(11)
N(21)–C(21)–S(21)	178.52(12)	N(22)–C(22)–S(22)	179.07(12)

Symmetry codes: (') 2 – x, –y, 1 – z; (") 1 – x, –y, 1 – z.

N(13)–C(16)–S(2) = 179.38(11)°, N(13)–C(16) = 1.1639(15), C(16)–S(2) = 1.6340(11) Å.

### 3.2.2. [Co(4-azpy)<sub>4</sub>(NCS)<sub>2</sub>](**2**) and [Mn(4-azpy)<sub>4</sub>(NCS)<sub>2</sub>](**3**)

The Mn(II) complex **3** is isomorphous to corresponding Co(II) complex **2**. Perspective views of **2** and **3**, together with the atom numbering schemes are presented in Figs. 2 and 3, and selected bond parameters are summarized in Tables 3 and 4, respectively. Each crystal structure consists of two crystallographically independent mononuclear and neutral metal(II) complexes. The metal centers are located on different inversion centers. The distorted octahedra around the metal centers are formed by N(py) donors of four 4-azidopyridine ligands and N donors of two terminal thiocyanato anions in *trans*-arrangement. The MN<sub>6</sub> chromophores have Co–N bond distances in the range from 2.071(5) to 2.221(5) Å and Mn–N bond lengths from 2.1690(12) to 2.3162(11) Å. The bond parameters of the terminal NCS<sup>–</sup> anions are within the following ranges: N–C–S angles from 178.1(5) to 179.6(4)°; N–C distances

from 1.158(7) to 1.168(7) Å; and C–S distances from 1.6261(14) to 1.639(6) Å. The crystallographically independent molecules differ mainly in their M(II)–N–C bond angles: 164.1(4) and 173.0(5)° for **2**, respectively 162.82(10)° and 171.73(11)° for **3**. The shortest metal–metal separations are 7.8896(7) and 7.9392(3) Å, for **2** and **3**, respectively.

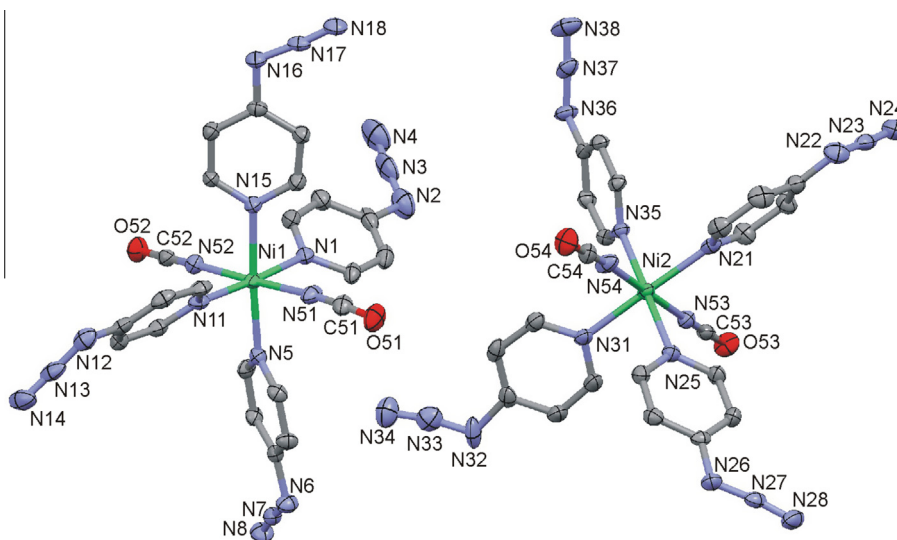
### 3.2.3. [Ni(4-azpy)<sub>4</sub>(NCO)<sub>2</sub>](**4**)

A perspective view of the two crystallographic different mononuclear and neutral complexes of **4**, together with the atom numbering scheme is given in Fig. 4, and selected bond lengths and bond angles are given in Table 5. Both Ni(II) centers are six-coordinated by N(py) atoms of four 4-azidopyridine molecules, and N atoms of two cyanato anions in *trans* dispositions. Each NiN<sub>6</sub> chromophore can be described as distorted octahedron with Ni–N(cyanato) bond distances in the range from 2.049(3) to 2.067(4) Å and longer Ni–N(py) bond lengths varying from 2.114(3) to 2.168(4) Å. The bond parameters of the terminal N-coordinated NCO<sup>–</sup> anions are: N–C–O angles from 177.7(5)° to 178.8(4)°; N–C distances from 1.155(5) to 1.173(5) Å; and C–O distances from 1.209(5) to 1.223(5) Å. The Ni–N–C angles of cyanate anions are 168.3(3)° and 175.4(4)° for Ni(1), whereas 170.4(3)° and 173.1(4)° for Ni(2). The shortest metal–metal separation is 8.0770(12) Å.

### 3.2.4. [Co(4-azpy)<sub>2</sub>(NCO)<sub>2</sub>](**5**)

A perspective view of **5**, together with the atom numbering scheme is given in Fig. 5, and selected bond lengths and bond angles are summarized in Table 6. The crystal structure of **5** consists of mononuclear and neutral Co(II) complexes. Co(1) is tetrahedrally coordinated by N(11) and N(12) of two terminal cyanato anions, further by N(1) and N(5) of two neutral 4-azidopyridine molecules. The Co(1)–N bond distances are in the range from 1.931(6) to 2.031(6) Å, and the N–Co(1)–N bond angles vary from 106.0(3)° to 120.4(3)°. The bond parameters of the terminal N-coordinated NCO<sup>–</sup> anions are: Co(1)–N–C = 162.8(6) and 167.8(6)°, N–C–O = 177.7(9) and 178.6(8)°; N–C = 1.145(9) and 1.174(10) Å, C–O = 1.187(10) and 1.206(9) Å. The shortest metal–metal separation is 5.5331(15) Å.

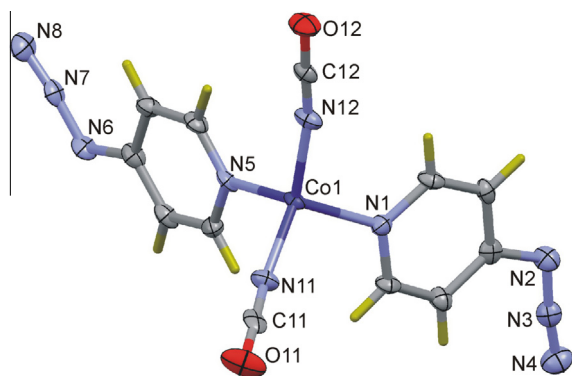
The 4-azidopyridine molecules in complexes **1–5** act exclusively as terminal ligands and are ligated via the pyridine-N donor atoms. The para-substituted covalent azide groups are practically co-planar to the plane of their pyridine rings (max. deviation: 16.9°), with N–N–N bond angles in the range from 169.9(6)° to 174.4(4)° and



**Fig. 4.** Perspective view of **4** together with the atom numbering scheme.

**Table 5**  
Selected bond lengths (Å) and angles (°) for compound **4**.

Ni(1)–N(1)	2.133(4)	Ni(2)–N(21)	2.168(4)
Ni(1)–N(5)	2.143(4)	Ni(2)–N(31)	2.159(4)
Ni(1)–N(11)	2.114(3)	Ni(2)–N(25)	2.141(3)
Ni(1)–N(15)	2.148(4)	Ni(2)–N(35)	2.127(3)
Ni(1)–N(51)	2.049(3)	Ni(2)–N(53)	2.067(4)
Ni(1)–N(52)	2.050(3)	Ni(2)–N(54)	2.054(4)
N(51)–C(51)	1.159(5)	C(51)–O(51)	1.217(5)
N(52)–C(52)	1.161(5)	C(52)–O(52)	1.209(5)
N(53)–C(53)	1.173(5)	C(53)–O(54)	1.214(5)
N(54)–C(54)	1.155(5)	C(54)–O(54)	1.223(5)
N(51)–Ni(1)–N(52)	178.12(14)	N(53)–Ni(2)–N(54)	179.44(15)
Ni(1)–N(51)–C(51)	175.4(4)	Ni(2)–N(53)–C(53)	173.1(3)
Ni(1)–N(52)–C(52)	168.8(3)	Ni(2)–N(54)–C(54)	170.4(3)
N(51)–C(51)–O(51)	177.7(5)	N(53)–C(53)–O(53)	178.8(4)
N(52)–C(52)–O(52)	177.8(5)	N(54)–C(54)–O(54)	178.2(5)

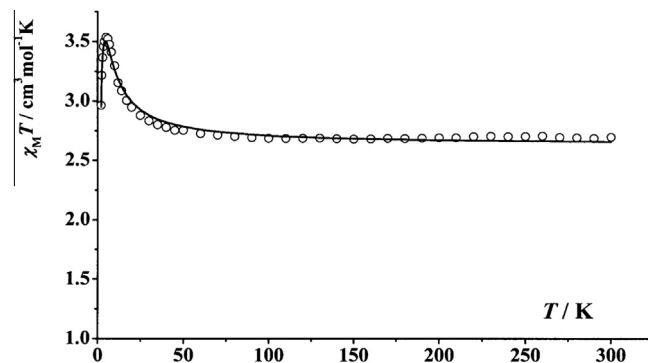
**Fig. 5.** Perspective view of **5** together with the atom numbering scheme.**Table 6**  
Selected bond lengths (Å) and angles (°) for compound **5**.

Co(1)–N(1)	2.021(6)	Co(1)–N(11)	1.931(6)
Co(1)–N(5)	2.031(6)	Co(1)–N(12)	1.939(6)
N(11)–C(11)	1.174(10)	C(11)–O(11)	1.187(10)
N(12)–C(12)	1.145(9)	C(12)–O(12)	1.206(9)
N(11)–Co(1)–N(12)	120.4(3)	N(11)–Co(1)–N(1)	106.0(3)
N(12)–Co(1)–N(1)	108.5(3)	N(11)–Co(1)–N(5)	107.0(3)
N(12)–Co(1)–N(5)	107.2(3)	N(1)–Co(1)–N(5)	107.1(2)
Co(1)–N(11)–C(11)	162.8(6)	Co(1)–N(12)–C(12)	167.8(6)
N(11)–C(11)–O(11)	178.6(8)	N(12)–C(12)–O(12)	177.7(9)

have asymmetric N–N bond distances [ $N\alpha$ – $N\beta$ : 1.223(5)–1.268(5) Å;  $N\beta$ – $N\gamma$ : 1.111(2)–1.149(6) Å;  $N\alpha$  bonded to carbon atom] (Table S1). Adjacent pyridine rings of 4-azidopyridine molecules form  $\pi$ – $\pi$  ring–ring interactions in compounds **2**, **3** and **5** with separations of their centers of gravity (Cg) less than 4.50 Å [compound **2**: ring (N1, C1–C5) with ring (N15, C16–C20) ( $2 - x, 1/2 + y, 1/2 - z$ ) = 4.239(4) Å; compound **3**: ring (N1, C1–C5) with ring (N11, C11–C15) = 4.271(1) Å; compound **5**: ring (N5, C6–C10) with ring (N5, C6–C10) ( $1 - x, 1 - y, 1 - z$ ) = 4.156(4) Å].

### 3.3. Magnetic properties of $[Ni_2(4\text{-azpy})_6(\text{NCS})_4]$ (**1**)

The magnetic properties of compound **1** in the form of  $\chi_M T$  vs.  $T$  plot are shown in Fig. 6. At room temperature, the  $\chi_M T$  value is  $2.69 \text{ cm}^3 \text{ K mol}^{-1}$ . This value is similar that the expected for two non-coupled  $S = 1$  ions ( $\chi_M T = 2.64 \text{ cm}^3 \text{ K mol}^{-1}$ ,  $g = 2.3$ ). When the samples are cooled,  $\chi_M T$  increases to a maximum of  $3.54 \text{ cm}^3 \text{ K mol}^{-1}$  at 5 K. Below 5 K, the  $\chi_M T$  value decreases abruptly to  $2.96 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K. This  $\chi_M T$  versus  $T$  plot is indicative of

**Fig. 6.** Plot of  $\chi_M T$  vs.  $T$  for compound **1**. The solid line represents the best fit curve (see text).

intramolecular ferromagnetic coupling with the presence of zero-field splitting parameter  $D$ . The magnetic data were fitted by using the PHI program [44] employing the spin-Hamiltonian  $H = -2J\hat{S}_1 \cdot \hat{S}_2 + D[\hat{S}_z^2 - 1/3(S+1)] + g\beta H\hat{S}_z$ . The calculated best fit parameters were  $2J = 3.11 \text{ cm}^{-1}$ ,  $D = 2.09 \text{ cm}^{-1}$ ,  $g = 2.29$ . The magnetically studied previously reported nickel(II) complexes with two bridging end-to-end thiocyanate ligands are few and in all of them the magnetic coupling is ferromagnetic. The  $J$  and  $D$  values found for complex **1** with double end-to-end bridging thiocyanate ligands are in agreement with those reported in the literature [17,45–49].

## 4. Conclusions

Five new metal(II) pseudohalide complexes with 4-azidopyridine (4-azpy) have been synthesized,  $[Ni_2(4\text{-azpy})_6(\text{NCS})_4]$  (**1**),  $[Co(4\text{-azpy})_4(\text{NCS})_2]$  (**2**),  $[Mn(4\text{-azpy})_4(\text{NCS})_2]$  (**3**),  $[Ni(4\text{-azpy})_4(\text{NCO})_2]$  (**4**), and  $[Co(4\text{-azpy})_2(\text{NCO})_2]$  (**5**), and characterized by IR, UV–Vis spectroscopy and single crystal X-ray diffraction. The crystal structure of the dimeric complex **1** features terminal and  $\mu(\text{N},\text{S})$ -bridging thiocyanates, and 4-azidopyridine ligands in *mer*-conformation around the distorted Ni(II) octahedra. The dimeric complex **1** exhibits intramolecular ferromagnetic coupling. The monomeric complexes **2–4** form distorted octahedral  $MN_6$  geometries with two N-coordinated terminal pseudohalides in *trans*-arrangement. The  $\text{CoN}_4$  tetrahedron in **5** is formed by two cyanate anions and two 4-azidopyridine molecules. The 4-azidopyridine molecules act exclusively as terminal ligands and are ligated via the pyridine-N donor atoms. The para-substituted covalent azide groups are practically co-planar to the plane of their pyridine rings and have asymmetric N–N bond distances. The results of this study clearly demonstrate that the nature of the central metal ion plays the major role in determining not only the stereochemical geometry which the metal ion will adapt but also the coordination bonding mode of the pseudohalide.

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## Appendix A. Supplementary data

CCDC 1010020–1010024 contains the supplementary crystallographic data for **1–5**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/contents/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: depos-

it@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2014.08.031>.

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