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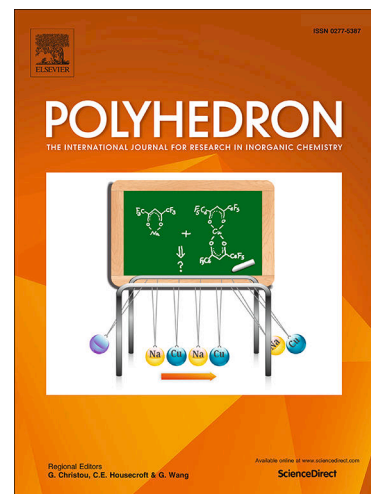
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# Azido and thiocyanato bridged dinuclear Ni(II) complexes involving 8-aminoquinoline based Schiff base as blocking ligands: Crystal structures, ferromagnetic properties and magneto-structural correlations

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## Abstract

The use of two 8-aminoquinoline-based tridentate N<sub>3</sub>-donor rigid Schiff base ligands (L1 and L2) with Ni(II) in the presence of the pseudohalides, NaN<sub>3</sub> and NaSCN results in the crystallization of the two novel Ni(II) dimers: [Ni<sub>2</sub>(L1)<sub>2</sub>(μ<sub>1,1'</sub>-N<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] (**1**) and [Ni<sub>2</sub>(L2)<sub>2</sub>(μ<sub>1,3</sub>-NCS)<sub>2</sub>(NCS)<sub>2</sub>] (**2**). Both complexes are centrosymmetric Ni(II) dimers where the Schiff base ligands coordinate the octahedral Ni(II) centres in a *mer* configuration with one terminal and two bridging pseudohalide ligands in the remaining positions. Complex **1** shows Ni(II) ions connected by a double μ<sub>1,1'</sub>-N<sub>3</sub><sup>-</sup> bridge whereas in complex **2** the Ni(II) ions are connected by a double μ<sub>1,3</sub>-NCS<sup>-</sup> bridge. The magnetic properties show the presence of a weak ferromagnetic

coupling in both compounds that can be fit with  $g = 2.290(6)$ ,  $J = 6.1(2) \text{ cm}^{-1}$ ,  $zJ' = -0.32(1) \text{ cm}^{-1}$  and  $|D| = 4.34(5) \text{ cm}^{-1}$  for **1** and  $g = 2.096(2)$ ,  $J = 4.71(5) \text{ cm}^{-1}$ ,  $zJ' = -0.054(2) \text{ cm}^{-1}$  and  $|D| = 1.52(2) \text{ cm}^{-1}$  for **2** (the Hamiltonian is written as  $-2JS_1S_2$ ). Both  $J$  values have been rationalized in terms of previous magneto structural correlations based on the Ni-N-Ni bridging angle in **1** and on the asymmetry of the Ni-S-C-N-Ni bridges in **2**.

**Keywords:** Schiff base; Ni(II); Azido/Thiocyanato; Crystal structure; Ferromagnetism.

## 1. Introduction

Di- and polynuclear transition metal based magnetic materials are widely studied due their application in various fields such as spintronics, information storage, molecular electronics, quantum computing, etc. In di- and polynuclear metal complexes, paramagnetic centres are bridged through small anionic ligands resulting in ferromagnetic (FM) or antiferromagnetic (AF) exchange interactions between the adjacent unpaired spins [1]. In FM interactions parallel alignments of the spins generate higher magnetic moments values and may give rise to single-molecule magnets (SMMs), single-chain magnets (SCMs), [2,3] ferromagnets and metamagnets. FM materials are designed based on judicious choice of metal ions, organic or inorganic blocking ligands and bridging units, [4] although in most cases, they have been achieved accidentally. Among the different bridging ligands, carboxylate and azide ions are the most investigated ones due to their versatile coordination and the magnetic behaviour of their compounds. These ligands can connect two or more metal ions in various bridging modes. In the azide ion the most common binding modes are  $\mu_{1,1'}$  (or end-on, EO) and  $\mu_{1,3}$  (or end-to-end, EE) [5-13] whereas bridging  $\mu_2\text{-}\eta^1:\eta^1$  *syn-syn*, *syn-anti*, and *anti-anti* are the most common bridging modes for carboxylate. Among the different magnetic materials, azido-bridged nickel(II) systems [14-39]

have been extensively studied and detailed magneto-structural correlations have been obtained based on their magnetic interactions [40,41]. Magneto-structural correlations reveals that double  $\mu_{1,3}$ -azido bridging leads to antiferromagnetic (AF) coupling, while double  $\mu_{1,1'}$  coordination is associated with ferromagnetic (F) exchange between the Ni(II) centres. In ferromagnetic interactions the Ni-N-Ni angle has a maximum value of  $104^\circ$ . There is only one exception, where low angles of  $\mu_{1,1'}$  bridging azido ligands lead to weak AF coupling [33].

In case of the thiocyanate ion, the common bridging mode is  $\mu_{1,3}$  [42-44] whereas  $\mu_{1,1'}$  binding mode is less common. Generally, double thiocyanato  $\mu_{1,3}$  bridged Ni(II) complexes exhibit ferromagnetic interactions. All the above information clearly shows that the diverse bonding modes of the bridging ligands and the nature of the blocking ligands around the paramagnetic centres are responsible for the structural and magnetic diversity of these Ni(II) complexes. Among the blocking ligands, Schiff-base ligands have been extensively used due to their ease of synthesis and rich coordination chemistry. A literature survey reveals that flexible, aliphatic amine-based Schiff-base ligands are generally utilized to synthesize paramagnetic di and polynuclear metal complexes. Whereas, rigid aminoquinoline based Schiff base ligands are rare in the literature. Few groups, including us, have used this type of ligands to prepare Cu(II), Ni(II), Cd(II) and Zn(II)-based complexes [45].

In the present work, two 8-aminoquinoline-based tridentate  $N_3$ -donor Schiff base ligands L1 and L2 (Scheme 1) have been reacted with Ni(II) salts in the presence of pseudohalides,  $NaN_3$  and  $NaSCN$ , respectively. We have isolated two dinuclear Ni(II) complexes:  $[Ni_2(L1)_2(\mu_{1,1'}-N_3)_2(N_3)_2]$  (**1**) and  $[Ni_2(L2)_2(\mu_{1,3}-NCS)_2(NCS)_2]$  (**2**). Here we report the structures and magnetic properties of these two new complexes showing ferromagnetic interactions between the metal centres.

## 2. Experimental section

### 2.1. Materials and physical measurements

All reagents and solvents are analytical grade chemicals and were purchased from commercial sources and used without further purification. Elemental analysis for C, H and N was carried out using a Perkin-Elmer 240C elemental analyser. Infrared spectra ( $400\text{-}4000\text{ cm}^{-1}$ ) were recorded with KBr pellets on a Nicolet Magna IR 750 series-II FTIR spectrophotometer.

The magnetic measurements were performed in a Quantum Design MPMS-XL-5 SQUID magnetometer in the 2-300 K temperature range with an applied magnetic field of 0.1 T on polycrystalline samples of compounds **1** and **2** (with masses of 27.741 and 24.182 mg, respectively). The susceptibility data were corrected for the sample holders, previously measured under the same conditions, and for the diamagnetic contributions as deduced by using Pascal's constant Tables [46].

### 2.2. X-ray crystallography

Single crystal X-ray data of complexes **1** and **2** were collected on a Bruker SMART APEX-II CCD diffractometer using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) at 150 K. Data processing, structure solution and refinement were performed using Bruker Apex-II suite program. All available reflections in  $2\theta_{\text{max}}$  range were harvested and corrected for Lorentz and polarization factors with Bruker SAINT plus [47]. Reflections were then corrected for absorption, inter-frame scaling, and other systematic errors with SADABS [48]. The structures were solved by direct methods and refined by means of full matrix least-square technique based on  $F^2$  with SHELX-2018/3 software package [49]. All the non-hydrogen atoms

were refined with anisotropic thermal parameters. C-H hydrogen atoms were inserted at geometrical positions with  $U_{\text{iso}} = 1/2U_{\text{eq}}$  to those they are attached. Crystal data and details of data collection and refinement for **1** and **2** are summarized in Table S1.

X-ray powder diffraction (XRPD) patterns were collected for polycrystalline samples of both compounds using a 0.5 mm glass capillary that was mounted and aligned on an Empyrean PANalytical powder diffractometer, using  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54177 \text{ \AA}$ ). A total of 4 scans were collected at room temperature in the  $2\theta$  range 5-40°.

### 2.3. Synthesis of the Schiff base ligands (L1 and L2)

The 8-aminoquinoline based Schiff base ligands are prepared by a reported procedure [45]. Briefly, a 1:1 molar ratio mixture of 2-pyridinecarboxaldehyde (for L1) or 2-acetylpyridine (for L2) and 8-aminoquinoline was taken in a round-bottom flask in methanol and refluxed for ~ 3 h. The so-obtained reddish yellow coloured solution was used directly for metal complex formation without further purification.

### 2.4. Synthesis of complex $[\text{Ni}_2(\text{L1})_2(\mu_{1,1}\text{-N}_3)_2(\text{N}_3)_2]$ (**1**)

A 5 mL methanolic solution of nickel nitrate hexahydrate (1.0 mmol, 291 mg) was added drop wise to 20 mL of a methanolic solution of L1 (1.0 mmol), followed by addition of sodium azide (2.0 mmol, 130 mg) and the resultant reaction mixture was stirred for *ca.* 4 h. Brown X-ray diffraction quality single crystals were obtained by slow evaporation of the solvent after few days. Yield: 586 mg (78 %). Anal. Calc. for  $\text{C}_{30}\text{H}_{22}\text{N}_{18}\text{Ni}_2$ : C 47.92 %; H 2.95 %; N 33.53 %; Found: C 47.15 %; H 2.81 %; N 33.01 %. IR ( $\text{cm}^{-1}$ , KBr):  $\nu(\text{N}_3^-)$  2011;  $\nu(\text{C}=\text{N})$  1625;  $\nu(\text{C}-\text{H})$  767. Phase purity was confirmed with X-ray powder diffraction (XRPD) that shows a perfect match with the simulated one from the single crystal X-ray structure (Fig. S1, see ESI).

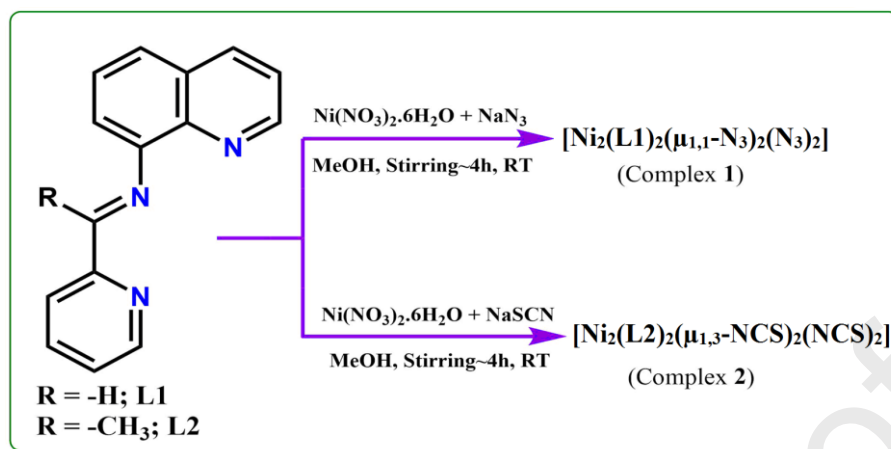
### 2.5 Synthesis of complex $[Ni_2(L2)_2(\mu_{1,3}-NCS)_2(NCS)_2]$ (**2**)

A 5 mL methanolic solution of nickel nitrate hexahydrate (1.0 mmol, 291 mg) was added drop wise to 20 mL of a methanolic solution of L2 (1.0 mmol), followed by addition of sodium thiocyanate (2.0 mmol, 162 mg) and the resultant reaction mixture was stirred for *ca.* 4 h. Brown colour X-ray diffraction quality single crystals were obtained by slow evaporation of the solvent after few days. Yield: 692 mg (82 %). Anal. Calc. for  $C_{36}H_{26}N_{10}Ni_2S_4$ : C 51.21 %; H 3.10 %; N 16.59 %; Found: C 50.97 %; H 2.81%; N 16.01 %. IR ( $cm^{-1}$ , KBr):  $\nu(NCS^-)$  2092;  $\nu(C=N)$  1615;  $\nu(C-H)$  779. Phase purity was confirmed with X-ray powder diffraction (XRPD) that shows a perfect match with the simulated one from the single crystal X-ray structure (Fig. S2, see ESI).

## 3. Results and discussion

### 3.1. Synthesis and characterization of complexes **1** and **2**

The 8-aminoquinoline based Schiff base ligands (L1 and L2) have been prepared following a standard procedure [45]. 2-pyridinecarboxaldehyde (for L1) or 2-acetylpyridine (for L2) is mixed with 8-aminoquinoline in 1:1 molar ratio in methanolic solution under refluxing condition (Scheme S1, ESI) to generate the corresponding Schiff base ligands. The ligands are directly used for complexation without further purification. Both complexes (**1** and **2**) are prepared by reacting  $Ni(NO_3)_2 \cdot 6H_2O$ , L1 (or L2) and  $NaN_3$  (or  $NaSCN$ ) in a 1:1:2 molar ratio in methanol under ambient conditions (Scheme 1). Both complexes crystallize after slow evaporation of the solvent. The FT-IR spectra of complexes **1** and **2** show the characteristic stretching frequencies of the azomethine group at around  $1600\text{ cm}^{-1}$  and the characteristic stretching frequency of  $N_3^-$  (in **1**) at  $2011\text{ cm}^{-1}$  and  $SCN^-$  (in **2**) at  $2092\text{ cm}^{-1}$  (Figs. S3 and S4, ESI) [50].



**Scheme 1.** Synthesis of complexes **1** and **2**.

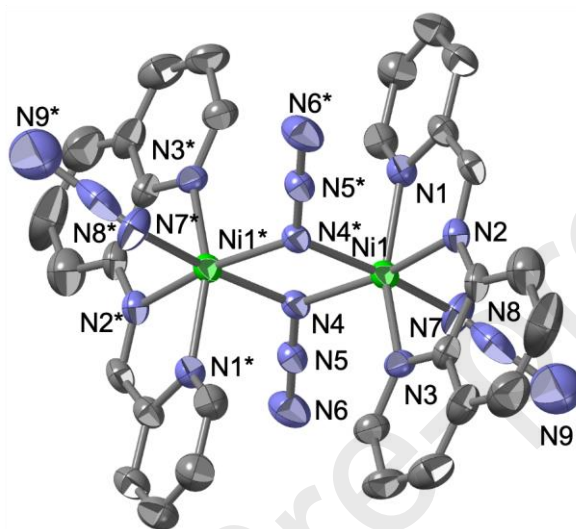
### 3.2. Crystal structure description of $[\text{Ni}_2(\text{L1})_2(\mu_{1,1}\text{-N}_3)_2(\text{N}_3)_2]$ (**1**)

Complex **1** crystallizes in the triclinic space group  $P\bar{1}$ . Its asymmetric unit contains one Ni centre, one Schiff base ligand (L1), one  $\mu_{1,1}\text{-N}_3^-$  bridging ligand and one terminal  $\text{N}_3^-$  ligand. The presence of an inversion centre generates the centrosymmetric complex **1** (Fig. 1).

The Ni(II) centres are hexacoordinated and show a distorted octahedral geometry. Continuous SHAPE<sup>48</sup> analysis shows that the Ni centre has a distorted octahedral environment (with a SHAPE coefficient of 1.768, Table S2, see ESI). The equatorial plane is formed by the imine nitrogen (N2) of L1, two N atoms: N4 and N4\* (\* = -x, -y, -z) from two symmetry related  $\mu_{1,1}\text{-N}_3$  bridges and the N atom (N7) of the terminal azido ligand. The axial positions are occupied by the quinoline (N3) and pyridine (N1) nitrogen atoms of the L1 ligand. Therefore, the Schiff base ligand coordinates the metal centre in the meridional configuration, with the remaining meridional positions occupied by azido ligands. The orientation of the ligands around the metal centres lead to an edge-sharing dioctahedral structure with a Ni...Ni distance of 3.305 Å. The Ni-N(imine), Ni-N(pyridine) and Ni-N(quinoline) bond distances vary within the

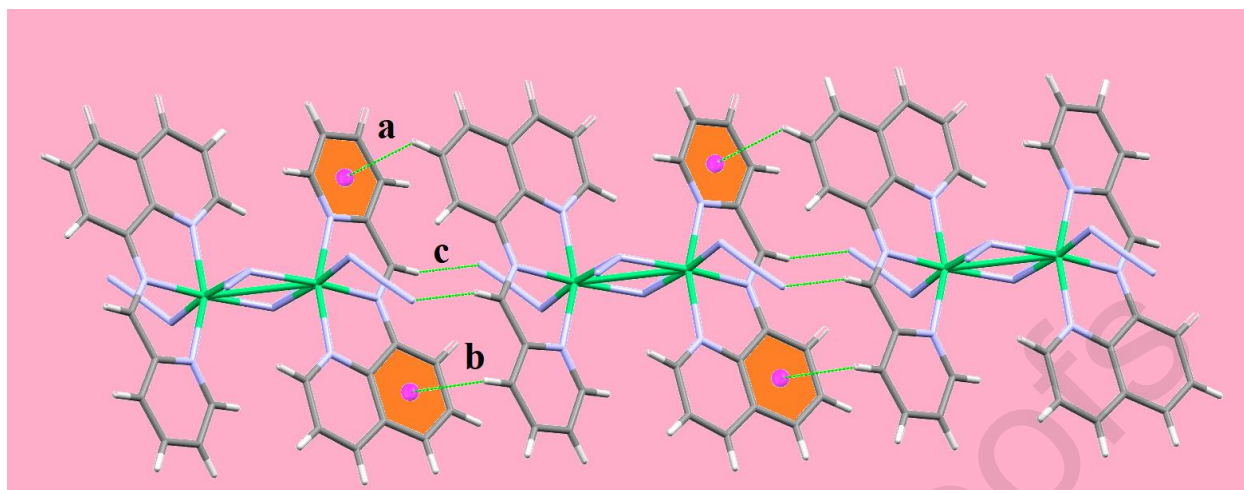


range 2.031(6)-2.103(6) Å whereas, Ni-N(azido) bond distances vary within the range 2.073(6)-2.180(6) Å (Table 1). The two Ni-N-Ni bridging angles are identical (101.0(3)°) and the central Ni(N)<sub>2</sub>Ni ring is planar. Both bridging and terminal azido ligands are nearly linear with N-N-N angles in the range 177.3(12)°-179.0(8)°, respectively.



**Fig. 1.** Crystal structure of complex **1**. Atoms are shown as 30 % thermal ellipsoids. H atoms are omitted for clarity. [\* = -x, -y, -z]

Adjacent dimers are connected by different supramolecular interactions as H-bonds and unconventional C-H $\cdots$  $\pi$  interactions with a shortest distance of 3.081 Å, forming chains along the *c* axis (Fig. 2).

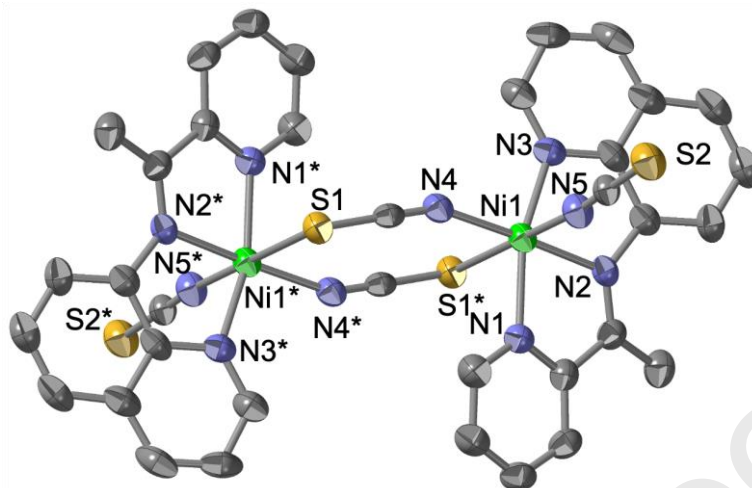


**Fig. 2.** Intermolecular H-bonds and unconventional C-H... $\pi$  interactions in complex **1** along the  $c$  axis [ $a = 3.081$  Å,  $b = 3.483$  Å and  $c = 2.376$  Å].

### 3.3. Crystal structure description of $[Ni_2(L2)_2(\mu_{1,3}\text{-NCS})_2(\text{NCS})_2]$ (**2**)

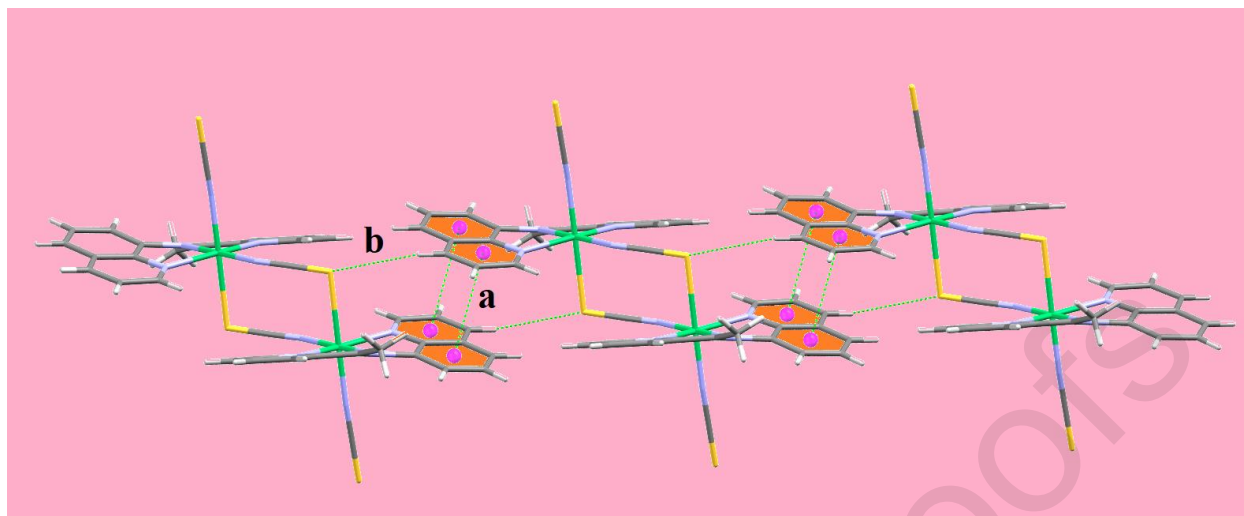
Complex **2** crystallizes in the triclinic space group  $P\bar{1}$ . Its asymmetric unit consists of one Ni centre, one Schiff base ligand (L2), one  $\mu_{1,3}\text{-SCN}^-$  bridging ligand and one terminal  $\text{SCN}^-$  ligand. The inversion centre generates the dimeric structure observed in **2** (Fig. 3).

The Ni(II) centres also show a distorted octahedral geometry (although less distorted than in complex **1**) with a SHAPE [51] coefficient of 1.620, (see ESI). The Ni(II) coordination sphere is of the type  $\text{NiN}_5\text{S}$ . The equatorial plane contains the imine N atom (N2) of the Schiff base, a N atom (N4) of one  $\mu_{1,3}$ -bridging thiocyanato group, a S atom (S1\*) [ $* = -x, -y, -z$ ] of the symmetry related  $\mu_{1,3}$ -bridging thiocyanato group and a N atom of the terminal thiocyanato ligand (N5). The axial positions are occupied by the quinoline nitrogen (N3) and the pyridine nitrogen (N1) atoms of the Schiff base ligand, L2. As in **1**, the Schiff base connects the metal centre with the meridional configuration, while the remaining meridional positions are occupied by the three thiocyanato ligands (two bridging and one terminal).



**Fig. 3.** Crystal structure of complex **2**. Atoms are shown as 50 % thermal ellipsoids. H atoms are omitted for clarity. [\* = -x, -y, -z]

The  $\mu_{1,3}$ -NCS<sup>-</sup> bridge is asymmetric with Ni-N and Ni-S bond distances of 2.013(3) Å and 2.6563(9) Å, respectively. The Ni...Ni distance through the double  $\mu_{1,3}$ -thiocyanato bridge is 5.539 Å. The terminal thiocyanato ligand is nearly linear with a N5-C18-S2 bond angle of 179.1(4)°. The Ni-N(imine), Ni-N(pyridine) and Ni-N(quinoline) bond distances vary within the range 2.032(3)-2.066(3) Å whereas, the Ni-N(thiocyanato) bond distances are 2.013(3) and 2.042(3) Å, respectively (Table 1). Supramolecular C-H...S and  $\pi$ ... $\pi$  interactions with shortest distances of 2.905 Å and 3.614 Å, respectively, connect adjacent dimers to generate chains of complexes of **2** along the *c* direction (Fig. 4).



**Fig. 4.** Unconventional intermolecular C-H...S and  $\pi$ ... $\pi$  interactions of complex **2** along the *ab* plane [*a* = 3.614 Å and *b* = 2.905 Å].

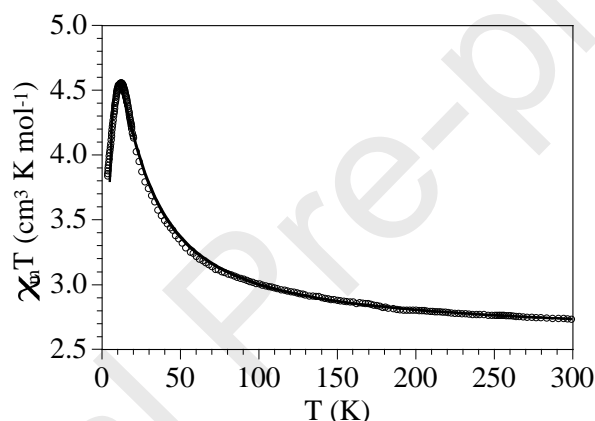
**Table 1** Selected bond lengths (Å) and angles (°) for complexes **1** and **2**.

<b>1</b>		<b>2</b>	
<b>Atoms</b>	<b>Length</b>	<b>Atoms</b>	<b>Length</b>
Ni-N1	2.103(6)	Ni-N1	2.066(3)
Ni-N2	2.031(6)	Ni-N2	2.032(3)
Ni-N3	2.086(6)	Ni-N3	2.060(3)
Ni-N4	2.073(6)	Ni-N4	2.013(3)
Ni-N4A	2.180(6)	Ni-N5	2.042(3)
Ni-N7	2.097(7)	Ni-S1	2.6563(9)
<b>Atoms</b>	<b>Angle</b>	<b>Atoms</b>	<b>angle</b>
Ni-N4-NiA	102.0(3)	N5-C18-S2	179.1(4)
Ni-N4A-NiA	102.0(3)	C17-S1-Ni	96.57(11)
N6-N5-N4	179.0(8)	C17-N4-Ni	155.2(3)
N9-N8-N7	177.3(12)	N4-Ni-S1	89.86(8)

### 3.4. Magnetic Properties

The product of the molar magnetic susceptibility per Ni(II) dimer ( $\chi_m T$ ) at room temperature for compound **1** is *ca.* 2.6 cm<sup>3</sup> K mol<sup>-1</sup>, which is the expected value for two Ni(II) ions with a *g* value of *ca.* 2.28 (Fig. 5). When the temperature is lowered,  $\chi_m T$  shows a continuous increase to reach a maximum of *ca.* 4.6 cm<sup>3</sup> K mol<sup>-1</sup> at *ca.* 12 K and a sharp decrease

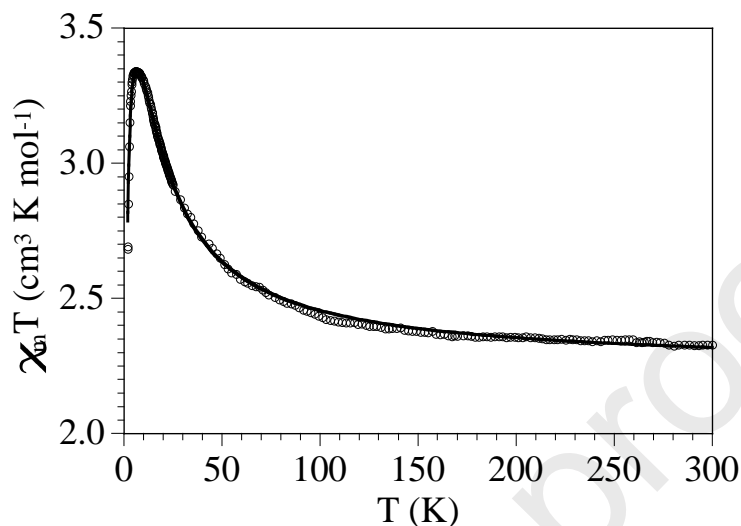
at lower temperatures to reach a value of ca.  $3.8 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K. The increase in  $\chi_m T$  indicates that the Ni(II) dimer has a weak Ni $\cdots$ Ni ferromagnetic coupling whereas the sharp decrease may be due to the presence of a zero field splitting (ZFS) of the Ni(II) ions and/or to a very weak interdimer antiferromagnetic interactions. Therefore, we have fit the magnetic properties to a simple model of a  $S = 1$  dimer with a ZFS including an interdimer coupling ( $zJ'$ ) using the PHI software.<sup>49</sup> This model reproduces satisfactorily the magnetic properties of compound **1** with  $g = 2.290(6)$ ,  $J = 6.1(2) \text{ cm}^{-1}$ ,  $zJ' = -0.32(1) \text{ cm}^{-1}$  and  $|D| = 4.34(5) \text{ cm}^{-1}$  (solid line in Fig. 5, the exchange Hamiltonian is written as  $-2JS_1S_2$ ).



**Fig. 5.** Thermal variation of the  $\chi_m T$  product for compound **1**. Solid line is the best fit to the model (see text).

Compound **2** shows a similar behaviour, with a  $\chi_m T$  value at room temperature of ca.  $2.3 \text{ cm}^3 \text{ K mol}^{-1}$ , the expected value for two independent Ni(II) ions with  $g$  ca. 2.1 (Fig. 6). When the sample is cooled, the  $\chi_m T$  product increases and reaches a maximum value of ca.  $4.6 \text{ cm}^3 \text{ K mol}^{-1}$  at ca. 10 K. At lower temperatures,  $\chi_m T$  shows a sharp decrease and reaches a value of ca.  $2.7 \text{ cm}^3 \text{ K mol}^{-1}$  at 2 K. This behaviour is very similar to that of compound **1** and, therefore, we have fit the magnetic properties with the same dimer model using the PHI software [52]. This model reproduces very satisfactorily the magnetic properties of compound **2** with  $g = 2.096(2)$ ,

$J = 4.71(5) \text{ cm}^{-1}$ ,  $zJ' = -0.054(2) \text{ cm}^{-1}$  and  $|D| = 1.52(2) \text{ cm}^{-1}$  (solid line in Fig. 6, the Hamiltonian is written as  $-2JS_1S_2$ ).



**Fig. 6.** Thermal variation of the  $\chi_m T$  product for compound **2**. Solid line is the best fit to the model (see text).

### 3.5. Magneto-structural correlations

The sign and strength of the exchange coupling constant ( $J$ ) between the paramagnetic centres is influenced by several structural parameters. It is well known that the bridging angle plays the most crucial role in determining the overall magnetic interactions. Ruiz et al. theoretically proved that doubly  $\mu_{1,1}$ -azido bridged dinickel(II) complexes exhibit ferromagnetic interactions when the Ni-N-Ni angles ( $\theta$ ) range from  $80^\circ$  to  $115^\circ$ , with  $J$  values increasing as the angle increases, reaching a maximum at around  $104^\circ$  and then decreasing with increasing  $\theta$  [40,41]. Most of the  $\mu_{1,1}$ -azido bridged dinuclear Ni(II) systems exhibit ferromagnetic coupling. [14-32, 34-39] There is only one example where a very low bridging angle of value  $90.4^\circ$  exhibits AF interaction between Ni(II) centres [33].

In complex **1** the Ni-N-Ni angle is  $101.0(3)^\circ$ , in the typical range for a ferromagnetic interaction, although, based only on the Ni-N-Ni bond angle, it is not possible to estimate a  $J$  value for compound **1**. Thus, whereas the Ni(II) complexes with double  $\mu_{1,1'}$ -N<sub>3</sub>-bridges [14-39] show Ni-N-Ni angles in the narrow range *ca.*  $98^\circ$ - $103.9^\circ$ , the  $J$  values show a large variation from  $1.9$  to  $36.3\text{ cm}^{-1}$  (assuming a  $-2JS_1S_2$  type Hamiltonian) with no clear relationship. This is confirmed by the fact that complexes [Ni(terpy)(N<sub>3</sub>)<sub>2</sub>] $\cdot$ H<sub>2</sub>O [16] and [Ni(pepci)(N<sub>3</sub>)<sub>2</sub>]<sub>2</sub> [26], with identical average angles ( $101.6^\circ$ ), show different  $J$  values ( $22.8$  and  $36.3\text{ cm}^{-1}$ , respectively). Furthermore, these two Ni(II) dimers show average angles very similar to compound **1** ( $101.0^\circ$ ) but show quite different  $J$  values ( $6.1\text{ cm}^{-1}$ ).

In contrast to  $\mu_{1,1'}$ -N<sub>3</sub> bridged Ni(II) complexes, magneto-structural correlations for  $\mu_{1,3}$ -thiocyanato bridged dinuclear Ni(II) systems are less explored. Ginsberg [53] and Hendrickson [54] followed the valence-bond theory based on Goodenough and Kanamori rules [55] of super exchange interactions or Anderson's expanded orbital theory [56] to explain ferromagnetic coupling in [(Ni<sub>2</sub>(en)<sub>4</sub>)( $\mu$ -NCS)<sub>2</sub>]<sub>2</sub>I<sub>2</sub>. In this theory, the ferromagnetism in the idealized structures is explained in terms of  $e_g||\sigma$ ,  $\pi||e_g'$  pathways. In the case of double  $\mu_{1,3}$ -NCS<sup>-</sup> bridged dinuclear Ni(II) systems, the ideal value of the Ni-N-C and Ni-S-C angles ( $180^\circ$  and  $90^\circ$ , respectively) result in zero orbital overlap and thus, in orthogonality of the orbitals, giving rise to a ferromagnetic coupling. Based on some azido, cyanato and thiocyanato bridged derivatives, [54] Hendrickson proposed that the differences in the magnetic behaviour are mainly controlled by two factors: (i) the Ni-S-C bond angle and (ii) the symmetry of the dimeric species, being more important the second factor. In the case of a symmetric bridge, the antiferromagnetic coupling is enhanced. Thiocyanato bridged complexes are weakly ferromagnetically coupled and the coupling is stronger with increasing asymmetry. In thiocyanato bridged complexes the geometry

is chair like and the molecular orbitals are always practically degenerated, facilitating the possibility of ferromagnetic coupling.

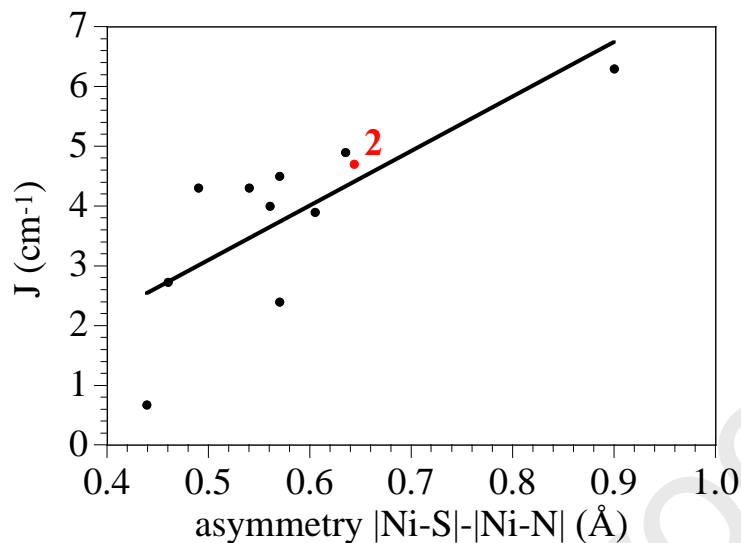
Table 2 shows the magnetic and crystallographic data of complex **2** and some Ni(II) dimers with a double  $\mu_{1,3}$ -NCS<sup>-</sup> bridge in order to discuss their magneto-structural trends. The last two examples are Ni(II) chains with a double  $\mu_{1,3}$ -NCS<sup>-</sup> bridge. Data in Table 2 reveal that even for significant deviations of the ideal values of the Ni-N-C and Ni-S-C bond angles (180° and 90°, respectively) the interactions are still ferromagnetic. In complex **2**, the values of the Ni-N-C and Ni-S-C bond angles (155.20° and 96.57°) are very close to those found in several other compounds with very similar J values. Furthermore, if we plot the variation of J with the asymmetry of the thiocyanate bridge, measured as the difference between the Ni-S and Ni-N bond distances, we can observe an approximate linear dependence (Fig. 7). In this relationship, the value of J observed for compound **2** is very close to the average trend.

**Table 2** Main structural (distances in Å and angles in degrees) and magnetic parameters for dinuclear and chain nickel(II) complexes with double  $\mu_{1,3}$ -thiocyanato bridging bond.

Compound	Ni-N	Ni-S	Ni-N-C	Ni-S-C	Ni...Ni	J (cm <sup>-1</sup> ) <sup>a</sup>	Ref.
Complex <b>2</b>	2.013	2.6563	155.20	96.57	5.539	4.7	This work
[{(Ni <sub>2</sub> (en) <sub>4</sub> )( $\mu$ -NCS) <sub>2</sub> ]}I <sub>2</sub>	2.04	2.61	167.0	100.0	5.708	4.5	57
[{Ni <sub>2</sub> (tren) <sub>2</sub> }( $\mu$ -NCS) <sub>2</sub> ](BPh <sub>4</sub> ) <sub>2</sub>	2.04	2.61	167.0	100.0	5.78	2.4	54
[{Ni(terpy)(NCS) <sub>2</sub> }] <sub>2</sub>	1.99	2.625	159.0	100.0	5.633	4.9	58
[{Ni <sub>2</sub> (2-methyl) <sub>3</sub> (NCS) <sub>2</sub> }( $\mu$ -NCS) <sub>2</sub> ]	2.06	2.55	165.2	100.7	5.656	4.3	59
[{Ni <sub>2</sub> (2-methyl) <sub>4</sub> }( $\mu$ -NCS) <sub>2</sub> ](PF <sub>6</sub> ) <sub>2</sub>	2.10	2.64	142.4	105.8			
[Ni <sub>2</sub> L <sub>2</sub> ( $\mu$ -SCN) <sub>2</sub> (SCN) <sub>2</sub> ].2H <sub>2</sub> O	1.93	2.83	166.7	96.20	5.785	6.3	59
[Ni <sub>2</sub> L <sub>2</sub> ( $\mu$ -SCN) <sub>2</sub> (SCN) <sub>2</sub> ].2H <sub>2</sub> O	2.030	2.635	162.4	102.67	5.750	3.9	17
[{Ni(L <sup>2</sup> )(SCN) <sub>2</sub> }] <sub>2</sub>	2.059	2.4981	164.18	105.13	5.781	0.67	43
Ni(NCS) <sub>2</sub> (HIm) <sub>2</sub>	2.038	2.5985	158.20	99.57	5.557	4.0	60
[Ni( $\mu_{N,S}$ -NCS)(dpt)(NCS)] <sub>2</sub>	2.11	2.57	163.74	102.54	5.736	2.73	61

<sup>a</sup>The J values correspond to the hamiltonian  $H = -2JS_1S_2$ .





**Fig. 7.** Variation of the coupling constant ( $J$ , with  $H = -JS_1S_2$ ) with the asymmetry of the thiocyanate bridge measured as the difference between the Ni-S and Ni-N bond distances.

#### 4. Conclusions

We have synthesized two novel dinuclear Ni(II) complexes with rigid 8-aminoquinoline based N<sub>3</sub>-donor Schiff base ligands [Ni<sub>2</sub>(L1)<sub>2</sub>(μ<sub>1,1'</sub>-N<sub>3</sub>)<sub>2</sub>(N<sub>3</sub>)<sub>2</sub>] (**1**) and [Ni<sub>2</sub>(L2)<sub>2</sub>(μ<sub>1,3</sub>-NCS)<sub>2</sub>(NCS)<sub>2</sub>] (**2**). Complex **1** is a double μ<sub>1,1'</sub>-azido bridged dimer whereas **2** is double μ<sub>1,3</sub>-thiocyanato bridged dimer. X-ray structure analyses reveal that the Ni(II) centres adopt a distorted octahedral geometry in both complexes with the Schiff base ligand binding the metal centre in a meridional fashion. The magnetic properties reveal a weak ferromagnetic coupling in both complexes that can be explained with magneto-structural correlations based on the Ni-N-Ni bond angles in **1** and with the asymmetry on the SCN bridge in complex **2**, measured as the difference between the Ni-S and Ni-N bond distances, since these distances are closely related to the Ni-S-C and Ni-N-C bond angles.

**Conflicts of interest**

There are no conflicts of interest to declare.

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**Appendix A. Supplementary data**

CCDC 1918387 and 1918388 contain the supplementary crystallographic data for complexes **1** and **2**, respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

## Notes and references

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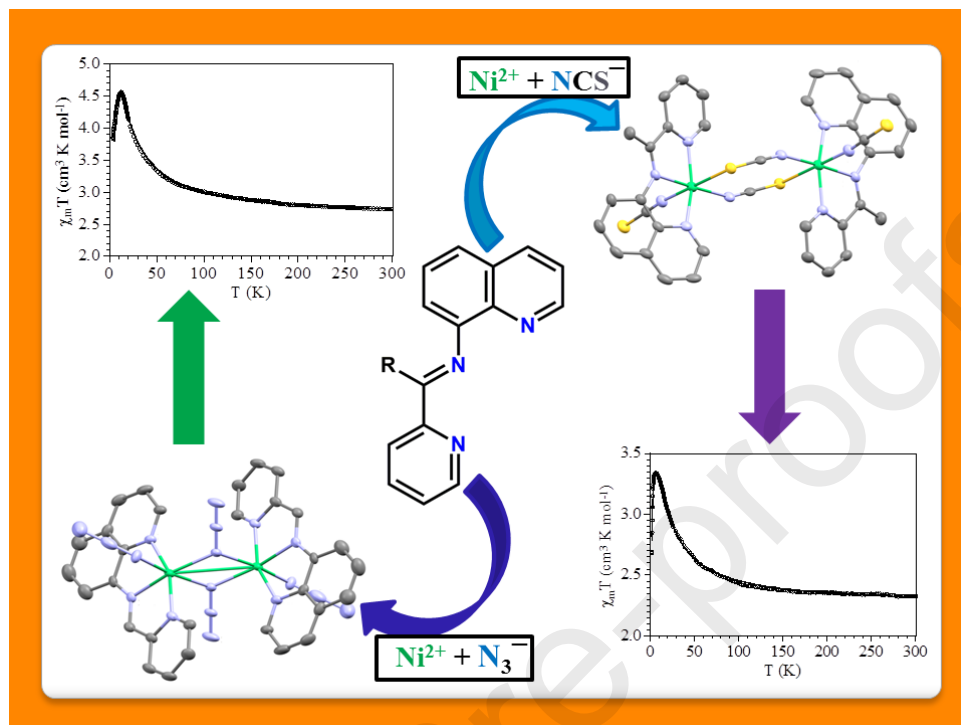
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**Table of Contents (TOC)**

We report two Ni(II) containing complexes with rigid 8-aminoquinoline based Schiff base ligands. Complexes **1** and **2** are thoroughly characterized by different spectroscopic techniques, elemental analysis and X-ray crystallography. Both dinuclear complexes exhibit a weak ferromagnetic coupling between the Ni(II) centres. Magneto-structural correlations based on Ni-N-Ni bond angles in **1** and in the asymmetry of the Ni-S and Ni-N bond angles in complex **2** are used to explain the magnitude and sign of the magnetic coupling.

### **Highlights**

- Schiff base
- Ni(II)
- Azido/Thiocyanato
- Crystal structure
- Ferromagnetism

Journal Pre-proofs

**CRediT author statement**

**Pravat Ghorai:** Investigation, Visualization **Paula Brandão:** Formal analysis **Samia Benmansour:** Formal analysis **Carlos J. Gómez García:** Formal analysis, Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration **Amrita Saha:** Writing - Original Draft, Writing - Review & Editing, Supervision, Project administration.