

Synthesis, crystal structure and thermal properties of *catena*-poly[[bis(4-methylpyridine)nickel(II)]-di- μ -thiocyanato], which shows an alternating all-*trans* and *cis-cis-trans*-coordination of the NiS₂N₂N₂^t octahedra (p = 4-methylpyridine, t = thiocyanate)

Christian Näther* and Sebastian Mangelsen

Institut für Anorganische Chemie, Universität Kiel, Max-Eyth.-Str. 2, 24118 Kiel, Germany. *Correspondence e-mail: cnaether@ac.uni-kiel.de

Received 5 June 2024

Accepted 17 June 2024

Edited by W. T. A. Harrison, University of Aberdeen, United Kingdom

Keywords: synthesis; crystal structure; coordination polymer; chain structure; thermal properties; nickel thiocyanate; 4-methylpyridine.

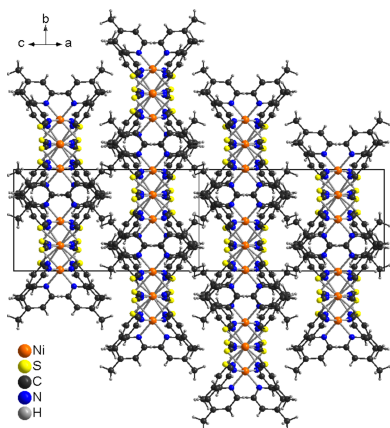
CCDC reference: 2363246

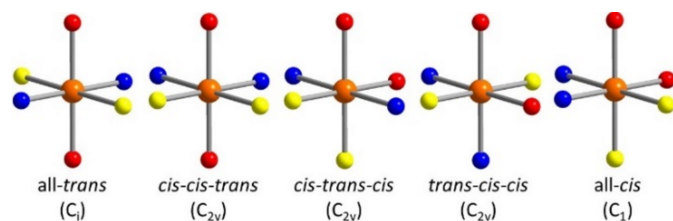
Supporting information: this article has supporting information at journals.iucr.org/e

The title compound, [Ni(NCS)₂(C₆H₇N)₂]_n, was prepared by the reaction of Ni(NCS)₂ with 4-methylpyridine in water. Its asymmetric unit consists of two crystallographically independent Ni^{II} cations, of which one is located on a twofold rotational axis whereas the second occupies a center of inversion, two independent thiocyanate anions and two independent 4-methylpyridine coligands in general positions. Each Ni^{II} cation is octahedrally coordinated by two 4-methylpyridine coligands as well as two N- and two S-bonded thiocyanate anions. One of the cations shows an all-*trans*, the other a *cis-cis-trans* configuration. The metal centers are linked by pairs of μ -1,3-bridging thiocyanate anions into [101] chains. X-ray powder diffraction shows that a pure crystalline phase has been obtained and thermogravimetry coupled to differential thermoanalysis reveals that the title compound loses half of the 4-methylpyridine coligands and transforms into Ni(NCS)₂(C₆H₇N). Nearly pure samples of this compound can be obtained by thermal annealing and a Rietveld refinement demonstrated that it is isotypic to its recently reported Cd analog [Neumann *et al.*, (2020). *CrystEngComm.* **22**, 184–194] In its crystal structure, the metal cations are linked by one μ -1,3(*N,S*)- and one μ -1,3,3(*N,S,S*)-bridging thiocyanate anion into single chains that condense *via* the μ -1,3,3(*N,S,S*)-bridging anionic ligands into double chains.

1. Chemical context

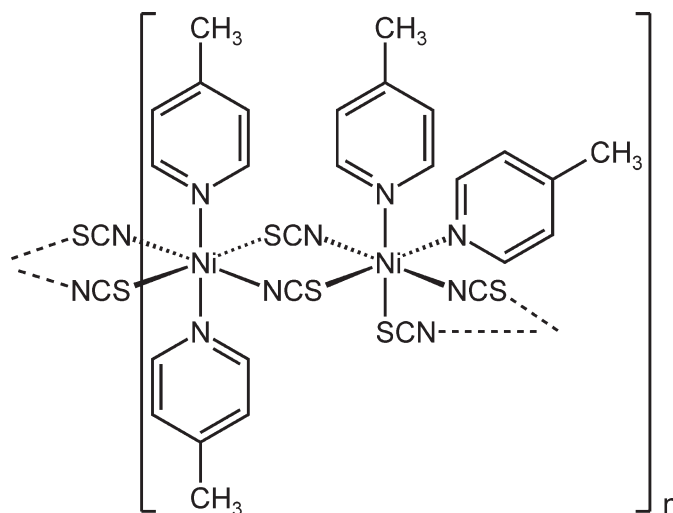
Coordination compounds based on transition-metal thiocyanates are an interesting class of compounds because they show an extremely large structural variability that can also lead to different polymorphs and isomers (Wöhlert *et al.*, 2013; Neumann *et al.*, 2018; Jochim *et al.*, 2020). This can be traced back to the fact that this anionic ligand shows many coordination modes (terminal, μ -1,1- and μ -1,3-bridging) and that compared to, *e.g.* azides, the coordinating donor atoms are different. Moreover, in many cases an octahedral coordination of the metal center is observed and in such compounds the metal cations are usually linked by pairs of anionic ligands into chains. Chain compounds are usually formed with mono-coordinating neutral coligands, whereas bridging coligands lead to the formation of layers. Five different isomeric configurations exist for such an octahedral coordination, including all-*trans* and all-*cis* and three different *cis-cis-trans* configurations (Fig. 1). In the majority of compounds, an all-*trans* configuration is observed but there are also examples of compounds in which the all-*cis*, *cis-cis-trans*, *cis-trans-cis* or *trans-cis-cis* configurations are present (see *Database survey*).




Figure 1

View of the different geometric isomers for an octahedral $MA_2B_2C_2$ coordination with the corresponding notation and idealized point group. The N atoms of the neutral co-ligands are shown in red.

The structural variability is further increased if such configurations alternate and in this context we have reported on compounds with the composition $Ni(NCS)_2(4\text{-chloropyridine})_2$ [Cambridge Structural Database (CSD) refcodes UHUVIF and UHUVIF01; Jochim *et al.*, 2018] and $Co(NCS)_2(4\text{-chloropyridine})_2$ (GIQQIJ and GIQQIJ01; Böhme *et al.*, 2020). For this compound, two different isomers were obtained, in both of which the Co^{II} cations are octahedrally coordinated and linked into chains by pairs of thiocyanate anions. However, in one of these isomers an all-*trans* configuration is present, leading to the formation of linear chains, whereas in the second an alternating all-*trans* and *cis-cis-trans* configuration is observed, which leads to the formation of corrugated chains. Solvent-mediated conversion experiments show that the isomer with corrugated chains is more stable than that with linear chains, which is surprising because, as mentioned above, most compounds form linear chains (Jochim *et al.*, 2018; Böhme *et al.*, 2020). In this context, it is noted that not only the metal configuration can alternate, because we have prepared the first $Co(NCS)_2$ coordination polymer with a linear chain structure in which an alternating fivefold and sixfold coordination is present (WEKVUH; Böhme *et al.*, 2022).

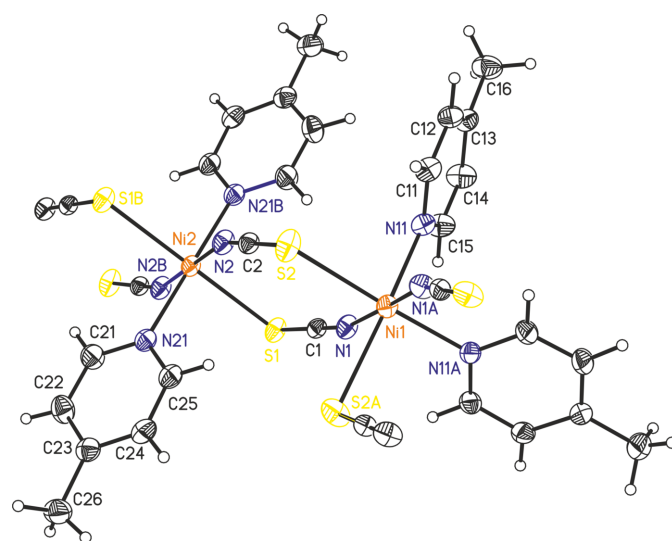


However, based on the results for the 4-chloropyridine compounds, we remembered the chloro–methyl exchange rule, which states that compounds with such ligands are very often structurally similar or even isotopic due to the fact that

the van der Waals radius of a methyl group is similar to that of a chlorine atom (Desiraju & Sarma, 1986). Consequently, we assumed that similar isomers might be prepared with 4-methylpyridine, C_6H_7N . Therefore, $Ni(NCS)_2$ was reacted with 4-methylpyridine, which leads to the formation of the title compound with the composition $Ni(NCS)_2(C_6H_7N)_2$, which is isotopic to the most stable isomer of $Ni(NCS)_2(4\text{-chloropyridine})_2$ and $Co(NCS)_2(4\text{-chloropyridine})_2$, which are already reported in the literature (Jochim *et al.*, 2018). We have not found any evidence for the formation of a metastable isomer with linear chains and 4-methylpyridine as ligand.

In this context it is mentioned that a compound with the stated composition $Ni(NCS)_2(C_6H_7N)_2$ is already reported in the CSD (QQQGJV; Solaculu *et al.*, 1974). This compound crystallizes in the orthorhombic space group $I222$ with the unusual value of $Z = 18$ formula units in the unit cell. Unfortunately, no atomic positions were presented and this entry is limited to unit-cell parameters, crystal system and space group. In fact, for this space group $Z = 16$ would be expected if two crystallographically independent formula units were present in the asymmetric unit, and in this case the volume for each non-hydrogen atom is calculated to be 23.2 \AA^3 , which is a relatively high value and might point to some solvent molecules being present. Therefore, from our point of view the existence of this crystalline form is at least questionable.

There is another entry in the CSD with this composition and for this structure atomic coordinates are available (ITMPNI; Lipowski & Andreotti, 1978). In this structure, each Ni^{II} cation is octahedrally coordinated by 4-methylpyridine coligands, two terminal N-bonded thiocyanate anions as well as one S- and one N-bonding bridging thiocyanate anion. Each two Ni^{II} cations are linked by pairs of μ -1,3-bridging anionic ligands into dinuclear complexes. Because the chemical composition is


Figure 2

Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 50% probability level. Symmetry codes (i) $-x + 1$, y , $-z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}$, $-y + \frac{1}{2}$, $-z + 1$.

Table 1

Selected geometric parameters (Å, °).

Ni1—N1	2.0358 (17)	Ni2—S1	2.5208 (5)
Ni1—S2	2.5653 (6)	Ni2—N2	2.0261 (17)
Ni1—N11	2.0956 (18)	Ni2—N21	2.1345 (18)
N1—Ni1—N1 ⁱ	174.18 (10)	S1—Ni2—S1 ⁱⁱ	180.0
S2—Ni1—S2 ⁱ	89.50 (3)	N2—Ni2—N2 ⁱⁱ	180.0
N11—Ni1—N11 ⁱ	89.52 (9)	N21—Ni2—N21 ⁱⁱ	180.0

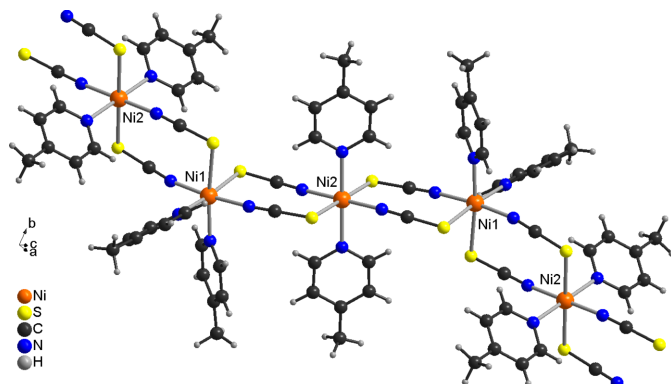
Symmetry codes: (i) $-x + 1, y, -z + \frac{1}{2}$; (ii) $-x + \frac{3}{2}, -y + \frac{1}{2}, -z + 1$.

identical to that of the title compound, it might be denoted as an isomer.

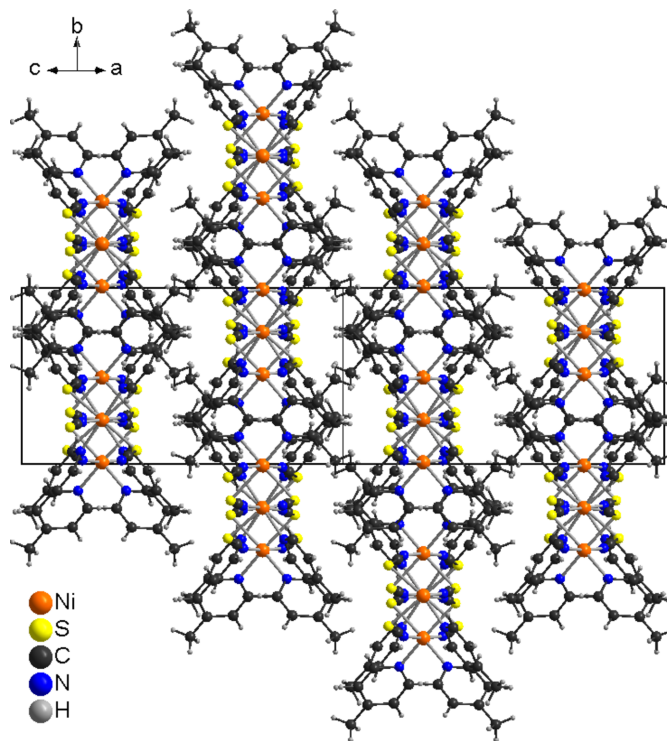
2. Structural commentary

The asymmetric unit of the title compound, $\text{Ni}(\text{NCS})_2(\text{C}_6\text{H}_7\text{N})_2$, consists of two crystallographically independent Ni^{II} cations, two crystallographically independent thiocyanate anions and two crystallographically independent 4-methylpyridine coligands (Fig. 2). Whereas the anionic and neutral ligands occupy general positions, one of the Ni^{II} cations (Ni1) is located on a crystallographic twofold rotation axis, and the second Ni^{II} cation (Ni2) occupies a center of inversion. Each of the Ni^{II} cations is sixfold coordinated by two N-bonding and two S-bonding μ -1,3-bridging thiocyanate anions as well as two 4-methylpyridine coligands. Ni2 shows an all-*trans* configuration whereas Ni1 is in a *cis-cis-trans* arrangement with the S-bonding thiocyanate anions and the 4-methylpyridine coligands in *cis* and the N-bonding thiocyanate in *trans* positions (Fig. 3). For the Ni^{II} cation that shows an all-*trans* coordination, the Ni—S bond lengths are a bit shorter, whereas the Ni—N distances to the coligands are slightly longer compared to the cation in the *cis-cis-trans* configuration (Table 1). The metal cations are linked by pairs of μ -1,3-bridging anionic ligands into chains that, because of the alternating all-*trans* and *cis-cis-trans* configurations of the metal ions, are corrugated (Fig. 3).

This compound is isotopic to the thermodynamically stable isomer of $\text{Ni}(\text{NCS})_2(4\text{-chloropyridine})_2$ (UHUVIF01; Böhme *et al.*, 2020), which indicates that the title compound is ther-

**Figure 3**

Crystal structure of the title compound with view of a chain and labeling of the Ni^{II} cations.

**Figure 4**

Crystal structure of the title compound with view along [101].

modynamically stable. This is further supported by the fact that in all of our synthetic work we never found hints that a further isomer could be prepared.

3. Supramolecular features

In the crystal structure of the title compound, the chains propagate along [101] with each chain surrounded by six neighboring chains (Fig. 4). There are no significant intermolecular C—H...N or C—H...S contacts and there are also no hints of any π - π stacking interactions.

4. Database survey

A search in the CSD (version 5.43, last update December 2023; Groom *et al.*, 2016) using CONQUEST (Bruno *et al.*, 2002) for compounds based on $\text{Ni}(\text{NCS})_2$ and 4-methylpyridine revealed that several such compounds have already been reported. This include the two compounds $\text{Ni}(\text{NCS})_2(\text{C}_6\text{H}_7\text{N})_2$ [QQQJIV (Solaculu *et al.*, 1974) and ITMPNI (Lipowski & Andreotti, 1978)], already mentioned in the *Chemical context* section and one chain compound with the same composition that crystallizes as a *p*-toluidine solvate (CECDET; Micu-Semeniuc *et al.*, 1983). For the latter compound, no atomic coordinates are given. All remaining compounds consist of discrete complexes with an octahedral Ni coordination including $\text{Ni}(\text{NCS})_2(\text{C}_6\text{H}_7\text{N})_4$ [ICMPNI01 (Kerr & Williams, 1977); ICMPNI03 (Soldatov *et al.*, 2004); ICMPNI (Andreotti *et al.*, 1972); ICMPNI02 (Harris *et al.*, 2001); ICMPNI04 and ICMPNI05 (Soldatov *et al.*, 2004) and

ICMPNI06 (Harris *et al.*, 2003)]. The majority of hits refer to clathrates of $\text{Ni}(\text{NCS})_2(\text{C}_6\text{H}_7\text{N})_4$, which are not listed in detail here.

At this point it is noted that this corresponds to a very rare coordination, because in most compounds with the general composition $M(\text{NCS})_2L_2$ (M = metal cation, L = coligand) an all-*trans* coordination is found, which leads to the formation of linear chains (Rams *et al.*, 2017a, 2020). Linear chains are also found for a *cis-cis-trans*-coordination, but only if the coligands are in the *trans*-position and the two N and two S-bonding thiocyanate anions are in the *cis*-position. This is the case in the isotopic compounds $M(\text{NCS})_2(4\text{-benzoylpyridine})_2$ with $M = \text{Co}, \text{Ni}$ [respectively, ODEYII (Rams *et al.*, 2017b) and GIQQUV (Jochim *et al.*, 2018)] or $\text{Co}(\text{NCS})_2(2,3\text{-dimethylpyrazine-1,4-dioxide})$ (refcode PEVZOG; Shi *et al.*, 2007). If the two bridging S-bonded thiocyanate anions are in *trans*-positions as in, *e.g.* $\text{Ni}(\text{NCS})_2(2,2'\text{-bipyridine})$ (GIOREG; Jochim *et al.*, 2018), or $\text{Mn}(\text{NCS})_2(4\text{-nitropyridine } N\text{-oxide})$ (SINKUW; Shi *et al.*, 2006a), the chains are corrugated. Corrugated chains are also observed if the two bridging N-bonded thiocyanate anions are in *trans*-positions and this is the case *e.g.* in $\text{Ni}(\text{NCS})_2[1\text{-}(2\text{-aminoethyl})\text{pyrrolidine-}N,N']$ (ABOBIC; Maji *et al.*, 2001). Finally, there are also examples for an all-*cis* configuration that also leads to the formation of corrugated chains and this includes *e.g.* $\text{Ni}(\text{NCS})_2(4\text{-methylpyridine } N\text{-oxide})$ [PEDSUN (Shi *et al.*, 2006b) and PEDSUN01 (Marsh, 2009)].

5. Additional investigations

Powder X-ray diffraction measurements demonstrate that the title compound was obtained as a pure phase (Fig. 5).

The title compound was also investigated by thermogravimetry and differential thermoanalysis (TG-DTA) measurements. Upon heating, several mass losses are

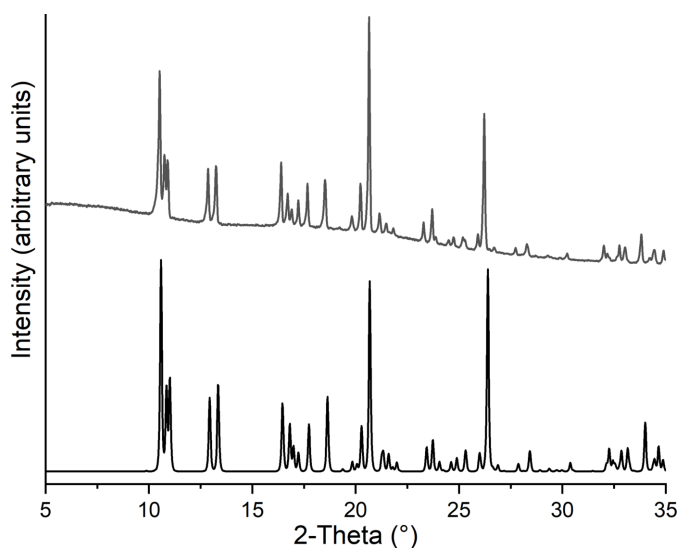


Figure 5
Experimental (top) and calculated (bottom) X-ray powder pattern of the title compound.

observed that are accompanied by endothermic events in the DTA curve (Fig. S1). From the DTG curve it is obvious that all mass losses are poorly resolved (Fig. S1). The experimental mass loss of the first and second steps is in rough agreement with that calculated for the removal of one 4-methylpyridine ligand in each step ($\Delta m_{\text{calc.}} = 17.0\%$), indicating that a more 4-methylpyridine-deficient compound with the composition $\text{Ni}(\text{NCS})_2(4\text{-methylpyridine})$ has formed.

Lowering the heating rate did not lead to better resolved curves and, therefore, isolation of this intermediate seems to be impossible. It was also not possible to prepare this phase from solution, even if an excess of Ni^{II} was used in the synthesis. Therefore, samples of the title compound were annealed for different times at different temperatures below the decomposition temperature observed in the TG-DTA measurements, until no reflections of the pristine compound **1** were present. In this case, a well-defined crystalline phase was obtained, for which the CN stretching vibrations of the anionic ligands are observed at 2118, 2141 and 2196 cm^{-1} , indicating that a more complex thiocyanate network has formed (Fig. S2). Unfortunately, indexing of this pattern did not lead to a reasonable unit cell but we reported the crystal structure of a compound with the composition $\text{Cd}(\text{NCS})_2(\text{C}_6\text{H}_7\text{N})$ a few years ago (Neumann *et al.*, 2020). Because Cd^{II} cations are much more chalcophilic than Ni^{II} cations, such compounds can easily be prepared and crystallized from solution. Based on the crystallographic data of $\text{Cd}(\text{NCS})_2(\text{C}_6\text{H}_7\text{N})$, a Rietveld refinement was performed for the residue obtained by thermal decomposition of the title compound, which proves that the Ni compound is isotopic and that this sample is contaminated with a small amount of $\text{Ni}(\text{NCS})_2$ [6.1 (3) wt.%], which might originate from a slightly too long tempering of the title compound (Fig. S3). In the crystal structure of $\text{Ni}(\text{NCS})_2(\text{C}_6\text{H}_7\text{N})$, the Ni^{II} cations are octahedrally coordinated by one 4-methylpyridine coligand, two N- and three S-bonding bridging thiocyanate anions (Fig. 6). The metal cations are

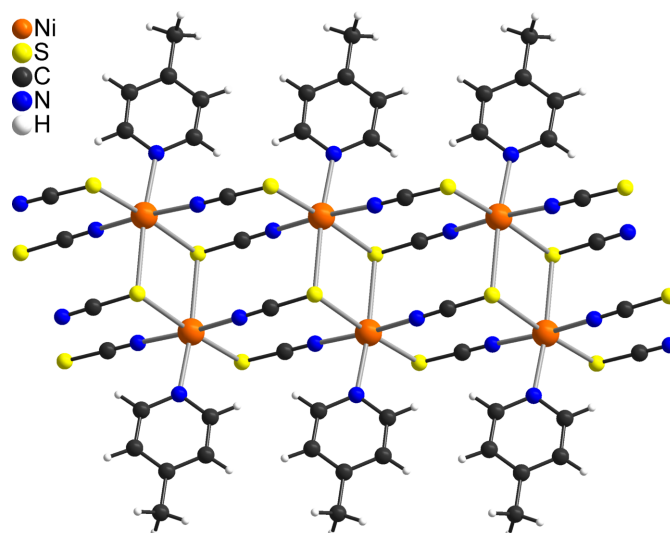


Figure 6
Crystal structure of $\text{Ni}(\text{NCS})_2(\text{C}_6\text{H}_7\text{N})$ obtained by thermal decomposition of the title compound.

linked by one μ -1,3(*N,S*)- and one μ -1,3,3(*N,S,S*)-bridging thiocyanate anion into single chains that condense *via* the μ -1,3,3(*N,S,S*)-bridging anionic ligands into double chains. The single chains are linked by each two S atoms sharing common edges, forming Ni₂S₂ rings.

Finally, it is noted that for the isotopic compounds with nickel and cobalt and 4-chloropyridine, no ligand-deficient compounds were detected and the reason for this difference in the thermal reactivity for isotopic compounds is not clear.

6. Synthesis and crystallization

Synthesis

4-Methylpyridine (purity 98%) and KNCS were obtained from Sigma-Aldrich and NiCl₂·6H₂O was purchased from Carl Roth.

6.00 mmol (1471 mg) of NiCl₂·6H₂O, 12.00 mmol (1160 mg) of KNCS and 12.00 mmol (1160 μ l) of 4-methylpyridine were stirred in 5 ml of demineralized water at room temperature for 1 day. The precipitate was filtered off, washed with demineralized water and dried in air. Single crystals of the title compound were obtained using the same molar ratio of the reactants without stirring. Elemental analysis for C₁₄H₁₄N₄NiS₂: calculated C 46.57, H 3.91, N 15.51; S 17.76, found C 46.78, H 4.08, N 15.72 S 17.94. The purity was also shown by powder X-ray diffraction (see Fig. S4). An IR spectrum of the title compound can be found in Fig. S4.

Experimental details

Elemental analysis was performed with a vario MICRO cube from Elementar Analysensysteme GmbH. IR spectra were recorded at room temperature on a Bruker Vertex70 FT-IR spectrometer using a broadband spectral range extension VERTEX FM for full mid and far IR. Thermogravimetry and differential thermoanalysis (TG-DTA) measurements were performed in a dynamic nitrogen atmosphere in Al₂O₃ crucibles with an 8°C min⁻¹ heating rate using a STA-PT 1000 thermobalance from Linseis. The TG-DTA instrument was calibrated using standard reference materials. X-ray powder diffraction experiments were performed using a Stoe STADI P transmission powder diffractometer with Cu K α 1 radiation (λ = 1.540598 Å), a Johann-type Ge(111) monochromator and a MYTHEN 1K detector from Dectris. The structure refinement was carried out using TOPAS Academic version 6.0 (Coelho, 2018). For the Rietveld refinement, the structure of Cd(NCS)₂(C₆H₇N) was used as starting model with Cd replaced by Ni. All ligands were set up as rigid bodies with bond lengths taken from the literature, including split positions for four carbon atoms to model rotational disorder of the ligand. The positions of the cation and all ligands were subject to unconstrained refinement, which quickly converged to a convincing R_{Bragg} of 1.2%.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The hydrogen atoms were positioned with idealized geometry (methyl H atoms allowed to

Table 2

Experimental details.

Crystal data	
Chemical formula	[Ni(NCS) ₂ (C ₆ H ₇ N) ₂]
M_r	361.12
Crystal system, space group	Monoclinic, C2/c
Temperature (K)	220
a, b, c (Å)	20.0352 (12), 9.1536 (5), 19.2268 (12)
β (°)	116.783 (6)
V (Å ³)	3147.8 (4)
Z	8
Radiation type	Mo K α
μ (mm ⁻¹)	1.50
Crystal size (mm)	0.16 × 0.12 × 0.08
Data collection	
Diffractometer	Stoe IPDS2
Absorption correction	Numerical (<i>X-RED</i> and <i>X-SHAPE</i> ; Stoe, 2008)
$T_{\text{min}}, T_{\text{max}}$	0.691, 0.864
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	15838, 3805, 3113
R_{int}	0.035
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.660
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.034, 0.091, 1.03
No. of reflections	3805
No. of parameters	195
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.48, -0.47

Computer programs: *X-AREA* (Stoe, 2008), *SHELXT2014/4* (Sheldrick, 2015a), *SHELXL2016/6* (Sheldrick, 2015b), *DIAMOND* (Brandenburg & Putz, 1999) and *XP* in *SHELXTL-PC* (Sheldrick, 2008) and *pubCIF* (Westrip, 2010).

rotate but not to tip) and were refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (1.5 for methyl H atoms) using a riding model.

Acknowledgements

This work was supported by the federal state of Schleswig-Holstein.

References

- Andreotti, G. D., Bocelli, G. & Sgarabotto, P. (1972). *Cryst. Struct. Commun.* **1**, 51–54.
- Böhme, M., Jochim, A., Rams, M., Lohmiller, T., Suckert, S., Schnegg, A., Plass, W. & Näther, C. (2020). *Inorg. Chem.* **59**, 5325–5338.
- Böhme, M., Rams, M., Krebs, C., Mangelsen, S., Jess, I., Plass, W. & Näther, C. (2022). *Inorg. Chem.* **61**, 16841–16855.
- Brandenburg, K. & Putz, H. (1999). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* **B58**, 389–397.
- Coelho, A. A. (2018). *J. Appl. Cryst.* **51**, 210–218.
- Desiraju, G. R. & Sarma, J. A. (1986). *Proc. - Indian Acad. Sci. Chem. Sci.* **96**, 599–605.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Harris, J. D., Eckles, W. E., Hepp, A. F., Duraj, S. A., Fanwick, P. E., Richardson, J. & Gordon, E. M. (2001). *Mater. Des.* **22**, 625–634.
- Harris, J. D., Eckles, W. E., Hepp, A. F., Duraj, S. A., Hehemann, D. G., Fanwick, P. E. & Richardson, J. (2003). *NASA Technical Reports*. 211890.

- Jochim, A., Rams, M., Böhme, M., Ceglarska, M., Plass, W. & Näther, C. (2020). *Dalton Trans.* **49**, 15310–15322.
- Jochim, A., Rams, M., Neumann, T., Wellm, C., Reinsch, H., Wójtowicz, G. M. & Näther, C. (2018). *Eur. J. Inorg. Chem.* pp. 4779–4789.
- Kerr, I. S. & Williams, D. J. (1977). *Acta Cryst.* **B33**, 3589–3592.
- Lipkowski, J. & Andreotti, G. D. (1978). *Transition Met Chem.* **3**, 117–121.
- Maji, T. K., Laskar, I. R., Mostafa, G., Welch, A. J., Mukherjee, P. S. & Chaudhuri, N. E. (2001). *Polyhedron*, **20**, 651–655.
- Marsh, R. E. (2009). *Acta Cryst.* **B65**, 782–783.
- Micu-Semeniuc, R., Hila, E., Dobos-Roman, G. & Ghergari, L. (1983). *Rev. Roum. Chim.* **28**, 471–475.
- Neumann, T., Ceglarska, M., Germann, L. S., Rams, M., Dinnebier, R. E., Suckert, S., Jess, I. & Näther, C. (2018). *Inorg. Chem.* **57**, 3305–3314.
- Neumann, T., Gallo, G., Jess, I., Dinnebier, R. E. & Näther, C. (2020). *CrystEngComm*, **22**, 184–194.
- Rams, M., Böhme, M., Kataev, V., Krupskaya, Y., Büchner, B., Plass, W., Neumann, T., Tomkowicz, Z. & Näther, C. (2017a). *Phys. Chem. Chem. Phys.* **19**, 24534–24544.
- Rams, M., Jochim, A., Böhme, M., Lohmiller, T., Ceglarska, M., Rams, M. M., Schnegg, A., Plass, W. & Näther, C. (2020). *Chem. A Eur. J.* **26**, 2837–2851.
- Rams, M., Tomkowicz, Z., Böhme, M., Plass, W., Suckert, S., Werner, J., Jess, I. & Näther, C. (2017b). *Phys. Chem. Chem. Phys.* **19**, 3232–3243.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Shi, J. M., Chen, J. N. & Liu, L. D. (2006a). *Pol. J. Chem.* **80**, 1909–1912.
- Shi, J. M., Li, W. N., Zhang, F. X., Zhang, X. & Liu, L. D. (2007). *Chin. J. Struct. Chem.* **26**, 118–121.
- Shi, J. M., Sun, Y. M., Liu, Z. & Liu, L. D. (2006b). *Chem. Phys. Lett.* **418**, 84–89.
- Solacolu, I., Sandulescu, D. & Dragulescu, C. (1974). *Rev. Roum. Chim.* **19**, 415–419.
- Soldatov, D. V., Enright, G. D. & Ripmeester, J. A. (2004). *Cryst. Growth Des.* **4**, 1185–1194.
- Stoe (2008). *X-Area, X-RED32 and X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Wöhlert, S., Jess, I., Englert, U. & Näther, C. (2013). *CrystEngComm*, **15**, 5326–5336.

supporting information

Acta Cryst. (2024). E80, 771-776 [https://doi.org/10.1107/S2056989024005887]

Synthesis, crystal structure and thermal properties of *catena*-poly[[bis(4-methylpyridine)nickel(II)]-di- μ -thiocyanato], which shows an alternating all-*trans* and *cis-cis-trans*-coordination of the NiS₂N^p₂N^t₂ octahedra (p = 4-methylpyridine, t = thiocyanate)

Christian Näther and Sebastian Mangelsen

Computing details

catena-Poly[[bis(4-methylpyridine- κ N)nickel(II)]-di- μ -thiocyanato- κ^2 N:S; κ^2 S:N]

Crystal data

[Ni(NCS)₂(C₆H₇N)₂]

$M_r = 361.12$

Monoclinic, C2/c

$a = 20.0352$ (12) Å

$b = 9.1536$ (5) Å

$c = 19.2268$ (12) Å

$\beta = 116.783$ (6)°

$V = 3147.8$ (4) Å³

$Z = 8$

$F(000) = 1488$

$D_x = 1.524$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 7998 reflections

$\theta = 2.4$ – 28.0 °

$\mu = 1.50$ mm⁻¹

$T = 220$ K

Block, green

$0.16 \times 0.12 \times 0.08$ mm

Data collection

Stoe IPDS-2
diffractometer

ω scans

Absorption correction: numerical
(X-Red and X-Shape; Stoe, 2008)

$T_{\min} = 0.691$, $T_{\max} = 0.864$

15838 measured reflections

3805 independent reflections

3113 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.035$

$\theta_{\max} = 28.0$ °, $\theta_{\min} = 2.4$ °

$h = -26 \rightarrow 26$

$k = -12 \rightarrow 12$

$l = -25 \rightarrow 25$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.034$

$wR(F^2) = 0.091$

$S = 1.03$

3805 reflections

195 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0616P)^2 + 0.1916P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.48$ e Å⁻³

$\Delta\rho_{\min} = -0.47$ e Å⁻³

Extinction correction: *SHELXL2016/6*

(Sheldrick, 2015b),

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.0034 (3)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.500000	0.49095 (4)	0.250000	0.02030 (11)
Ni2	0.750000	0.250000	0.500000	0.02012 (11)
S1	0.66327 (3)	0.42321 (6)	0.52157 (3)	0.02554 (14)
C1	0.60061 (10)	0.4565 (2)	0.43118 (11)	0.0199 (4)
N1	0.55720 (9)	0.4797 (2)	0.36824 (10)	0.0240 (4)
S2	0.58017 (3)	0.29192 (7)	0.23054 (3)	0.03120 (15)
C2	0.64768 (11)	0.2743 (2)	0.31946 (11)	0.0213 (4)
N2	0.69454 (10)	0.2631 (2)	0.38228 (10)	0.0256 (4)
N11	0.57268 (9)	0.6535 (2)	0.24781 (9)	0.0230 (3)
C11	0.59509 (11)	0.6616 (2)	0.19194 (11)	0.0260 (4)
H11	0.576619	0.592325	0.151505	0.031*
C12	0.64407 (12)	0.7668 (2)	0.19100 (12)	0.0271 (4)
H12	0.657378	0.769083	0.149963	0.033*
C13	0.67375 (11)	0.8695 (2)	0.25052 (12)	0.0264 (4)
C14	0.64970 (13)	0.8611 (3)	0.30801 (13)	0.0332 (5)
H14	0.667379	0.928794	0.349211	0.040*
C15	0.60000 (13)	0.7538 (3)	0.30461 (13)	0.0308 (5)
H15	0.584526	0.750894	0.344048	0.037*
C16	0.72901 (14)	0.9821 (3)	0.25378 (16)	0.0391 (6)
H16A	0.758663	0.943774	0.229594	0.059*
H16B	0.761580	1.006536	0.307691	0.059*
H16C	0.702696	1.069001	0.226168	0.059*
N21	0.68081 (9)	0.0707 (2)	0.49738 (10)	0.0246 (4)
C21	0.70854 (12)	-0.0404 (3)	0.54745 (13)	0.0313 (5)
H21	0.760343	-0.043195	0.579938	0.038*
C22	0.66472 (13)	-0.1516 (3)	0.55383 (13)	0.0343 (5)
H22	0.686953	-0.227367	0.590015	0.041*
C23	0.58782 (12)	-0.1514 (3)	0.50670 (13)	0.0286 (4)
C24	0.55988 (12)	-0.0385 (3)	0.45291 (13)	0.0298 (5)
H24	0.508574	-0.034966	0.418356	0.036*
C25	0.60707 (11)	0.0684 (3)	0.44994 (12)	0.0277 (4)
H25	0.586557	0.143308	0.412862	0.033*
C26	0.53820 (14)	-0.2658 (3)	0.51501 (16)	0.0367 (5)
H26A	0.548385	-0.359533	0.498245	0.055*
H26B	0.486273	-0.239712	0.483032	0.055*
H26C	0.547883	-0.272090	0.569101	0.055*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01658 (17)	0.0244 (2)	0.01412 (17)	0.000	0.00174 (13)	0.000
Ni2	0.01671 (17)	0.0250 (2)	0.01461 (17)	0.00380 (13)	0.00348 (13)	0.00186 (12)
S1	0.0231 (2)	0.0337 (3)	0.0144 (2)	0.00884 (19)	0.00373 (17)	0.00084 (18)
C1	0.0179 (8)	0.0198 (9)	0.0215 (9)	0.0000 (7)	0.0084 (7)	-0.0027 (7)
N1	0.0205 (7)	0.0295 (10)	0.0168 (8)	0.0044 (6)	0.0039 (6)	0.0002 (6)
S2	0.0295 (3)	0.0368 (3)	0.0162 (2)	0.0087 (2)	0.00049 (19)	-0.00435 (19)
C2	0.0220 (8)	0.0213 (10)	0.0218 (9)	0.0017 (7)	0.0109 (7)	-0.0009 (7)
N2	0.0235 (8)	0.0316 (10)	0.0179 (8)	0.0068 (7)	0.0060 (6)	0.0016 (6)
N11	0.0201 (7)	0.0262 (9)	0.0215 (7)	-0.0024 (6)	0.0084 (6)	-0.0045 (6)
C11	0.0241 (9)	0.0308 (11)	0.0211 (9)	-0.0018 (8)	0.0085 (7)	-0.0070 (8)
C12	0.0280 (9)	0.0313 (11)	0.0254 (10)	-0.0007 (8)	0.0149 (8)	-0.0028 (8)
C13	0.0229 (9)	0.0270 (11)	0.0296 (10)	-0.0005 (8)	0.0121 (8)	-0.0025 (8)
C14	0.0373 (11)	0.0352 (13)	0.0303 (10)	-0.0109 (10)	0.0182 (9)	-0.0137 (9)
C15	0.0354 (11)	0.0333 (12)	0.0284 (10)	-0.0082 (9)	0.0187 (9)	-0.0121 (8)
C16	0.0417 (13)	0.0357 (14)	0.0477 (15)	-0.0113 (10)	0.0272 (12)	-0.0077 (10)
N21	0.0210 (7)	0.0274 (10)	0.0236 (8)	0.0025 (6)	0.0084 (6)	0.0006 (6)
C21	0.0234 (9)	0.0334 (12)	0.0304 (11)	0.0012 (9)	0.0062 (8)	0.0051 (9)
C22	0.0353 (11)	0.0305 (12)	0.0308 (11)	0.0021 (9)	0.0091 (9)	0.0054 (9)
C23	0.0318 (10)	0.0273 (11)	0.0308 (10)	-0.0014 (8)	0.0177 (8)	-0.0071 (8)
C24	0.0224 (9)	0.0336 (12)	0.0316 (11)	0.0018 (8)	0.0105 (8)	-0.0036 (9)
C25	0.0232 (9)	0.0317 (12)	0.0261 (10)	0.0037 (8)	0.0094 (8)	0.0006 (8)
C26	0.0397 (12)	0.0333 (13)	0.0450 (13)	-0.0061 (10)	0.0260 (11)	-0.0074 (10)

Geometric parameters (\AA , $^\circ$)

Ni1—N1	2.0358 (17)	C13—C14	1.393 (3)
Ni1—N1 ⁱ	2.0358 (17)	C13—C16	1.493 (3)
Ni1—S2 ⁱ	2.5653 (6)	C14—H14	0.9400
Ni1—S2	2.5653 (6)	C14—C15	1.379 (3)
Ni1—N11 ⁱ	2.0955 (17)	C15—H15	0.9400
Ni1—N11	2.0956 (18)	C16—H16A	0.9700
Ni2—S1 ⁱⁱ	2.5208 (5)	C16—H16B	0.9700
Ni2—S1	2.5208 (5)	C16—H16C	0.9700
Ni2—N2	2.0261 (17)	N21—C21	1.337 (3)
Ni2—N2 ⁱⁱ	2.0262 (17)	N21—C25	1.342 (3)
Ni2—N21	2.1345 (18)	C21—H21	0.9400
Ni2—N21 ⁱⁱ	2.1345 (18)	C21—C22	1.385 (3)
S1—C1	1.6501 (19)	C22—H22	0.9400
C1—N1	1.148 (3)	C22—C23	1.392 (3)
S2—C2	1.6414 (19)	C23—C24	1.389 (3)
C2—N2	1.153 (3)	C23—C26	1.501 (3)
N11—C11	1.340 (3)	C24—H24	0.9400
N11—C15	1.340 (3)	C24—C25	1.380 (3)
C11—H11	0.9400	C25—H25	0.9400
C11—C12	1.381 (3)	C26—H26A	0.9700

C12—H12	0.9400	C26—H26B	0.9700
C12—C13	1.390 (3)	C26—H26C	0.9700
N1—Ni1—N1 ⁱ	174.18 (10)	C11—C12—H12	119.9
N1 ⁱ —Ni1—S2	82.84 (5)	C11—C12—C13	120.2 (2)
N1—Ni1—S2 ⁱ	82.84 (5)	C13—C12—H12	119.9
N1 ⁱ —Ni1—S2 ⁱ	93.01 (5)	C12—C13—C14	116.3 (2)
N1—Ni1—S2	93.01 (5)	C12—C13—C16	122.4 (2)
N1—Ni1—N11 ⁱ	93.45 (7)	C14—C13—C16	121.3 (2)
N1 ⁱ —Ni1—N11 ⁱ	90.68 (7)	C13—C14—H14	119.9
N1—Ni1—N11	90.68 (7)	C15—C14—C13	120.1 (2)
N1 ⁱ —Ni1—N11	93.45 (7)	C15—C14—H14	119.9
S2—Ni1—S2 ⁱ	89.50 (3)	N11—C15—C14	123.2 (2)
N11 ⁱ —Ni1—S2 ⁱ	90.86 (5)	N11—C15—H15	118.4
N11—Ni1—S2	90.85 (5)	C14—C15—H15	118.4
N11 ⁱ —Ni1—S2	173.52 (5)	C13—C16—H16A	109.5
N11—Ni1—S2 ⁱ	173.52 (5)	C13—C16—H16B	109.5
N11—Ni1—N11 ⁱ	89.52 (9)	C13—C16—H16C	109.5
S1—Ni2—S1 ⁱⁱ	180.0	H16A—C16—H16B	109.5
N2—Ni2—S1 ⁱⁱ	85.71 (5)	H16A—C16—H16C	109.5
N2 ⁱⁱ —Ni2—S1	85.71 (5)	H16B—C16—H16C	109.5
N2—Ni2—S1	94.29 (5)	C21—N21—Ni2	120.87 (14)
N2 ⁱⁱ —Ni2—S1 ⁱⁱ	94.29 (5)	C21—N21—C25	116.78 (19)
N2—Ni2—N2 ⁱⁱ	180.0	C25—N21—Ni2	122.18 (15)
N2 ⁱⁱ —Ni2—N21	90.24 (7)	N21—C21—H21	118.4
N2—Ni2—N21 ⁱⁱ	90.23 (7)	N21—C21—C22	123.25 (19)
N2—Ni2—N21	89.76 (7)	C22—C21—H21	118.4
N2 ⁱⁱ —Ni2—N21 ⁱⁱ	89.77 (7)	C21—C22—H22	120.0
N21 ⁱⁱ —Ni2—S1 ⁱⁱ	89.95 (5)	C21—C22—C23	120.1 (2)
N21 ⁱⁱ —Ni2—S1	90.05 (5)	C23—C22—H22	120.0
N21—Ni2—S1 ⁱⁱ	90.05 (5)	C22—C23—C26	121.4 (2)
N21—Ni2—S1	89.95 (5)	C24—C23—C22	116.3 (2)
N21—Ni2—N21 ⁱⁱ	180.0	C24—C23—C26	122.3 (2)
C1—S1—Ni2	101.33 (7)	C23—C24—H24	119.8
N1—C1—S1	179.8 (2)	C25—C24—C23	120.31 (19)
C1—N1—Ni1	164.70 (17)	C25—C24—H24	119.8
C2—S2—Ni1	101.18 (7)	N21—C25—C24	123.2 (2)
N2—C2—S2	179.1 (2)	N21—C25—H25	118.4
C2—N2—Ni2	162.45 (17)	C24—C25—H25	118.4
C11—N11—Ni1	122.82 (14)	C23—C26—H26A	109.5
C11—N11—C15	117.01 (18)	C23—C26—H26B	109.5
C15—N11—Ni1	120.16 (14)	C23—C26—H26C	109.5
N11—C11—H11	118.5	H26A—C26—H26B	109.5
N11—C11—C12	123.06 (19)	H26A—C26—H26C	109.5
C12—C11—H11	118.5	H26B—C26—H26C	109.5
Ni1—N11—C11—C12	-178.77 (16)	C15—N11—C11—C12	0.0 (3)
Ni1—N11—C15—C14	178.07 (19)	C16—C13—C14—C15	-178.4 (2)

Ni2—N21—C21—C22	173.01 (19)	N21—C21—C22—C23	0.0 (4)
Ni2—N21—C25—C24	-172.91 (17)	C21—N21—C25—C24	2.4 (3)
N11—C11—C12—C13	1.2 (3)	C21—C22—C23—C24	2.3 (3)
C11—N11—C15—C14	-0.8 (3)	C21—C22—C23—C26	-176.7 (2)
C11—C12—C13—C14	-1.7 (3)	C22—C23—C24—C25	-2.2 (3)
C11—C12—C13—C16	177.7 (2)	C23—C24—C25—N21	-0.1 (4)
C12—C13—C14—C15	1.0 (3)	C25—N21—C21—C22	-2.4 (3)
C13—C14—C15—N11	0.2 (4)	C26—C23—C24—C25	176.8 (2)

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