# Crystal structure of pyridinium tetraisothiocyanatodipyridinechromium(III) pyridine monosolvate

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In the crystal structure of the title compound, $(C_5H_6N)[Cr(NCS)_4(C_5H_5N)_2]\cdot C_5H_5N$, the $Cr^{III}$ ions are octahedrally coordinated by four $N$-bonding thiocyanate anions and two pyridine ligands into discrete negatively charged complexes, with the $Cr^{III}$ ion, as well as the two pyridine ligands, located on crystallographic mirror planes. The mean planes of the two pyridine ligands are rotated with respect to each other by 90°. Charge balance is achieved by one protonated pyridine molecule that is hydrogen bonded to one additional pyridine solvent molecule, with both located on crystallographic mirror planes and again rotated by exactly 90°. The pyridinium H atom was refined as disordered between both pyridine N atoms in a 70:30 ratio, leading to a linear N—H···N hydrogen bond. In the crystal, discrete complexes are linked by weak C—H···S hydrogen bonds into chains that are connected by additional C—H···S hydrogen bonding via the pyridinium cations and solvent molecules into layers and finally into a three-dimensional network.
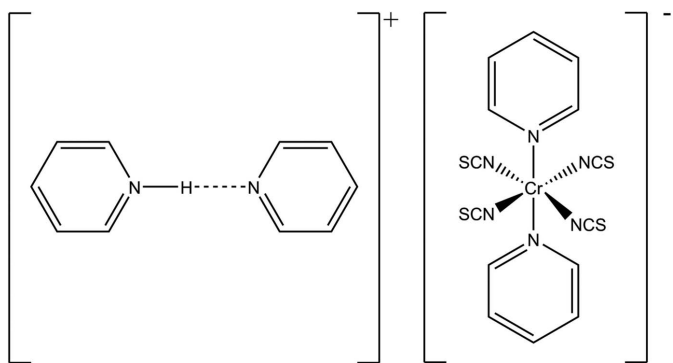
## 1. Chemical context

Coordination compounds with paramagnetic transition metals are of great interest because of their diverse magnetic properties (Cirera *et al.*, 2009; Giannopoulos *et al.*, 2014; Glaser, 2011; Yuan *et al.*, 2007). Those in which the metal cations are linked by small-sized ligands that can mediate magnetic exchange are of special importance because co-operative magnetic phenomena can be expected. Prominent examples for this class of ligands are azides, oxalates and cyanides (Wang *et al.*, 2005, 2008; Zhang *et al.*, 2012; Manson *et al.*, 2005; Ding *et al.*, 2012). In this context also, thiocyanate ligands are useful because they show a large variety of coordination modes, with the $\mu$-1,3-bridging mode as the most important (Jochim *et al.*, 2018; Mautner *et al.*, 2016, 2017; Shurdha *et al.*, 2013; Mekuimemba *et al.*, 2018; Wöhlert *et al.*, 2014a; Werner *et al.*, 2015). It is noted that these compounds are frequently difficult to prepare because terminal $N$-coordination is usually preferred for $3d$ metal cations. Nevertheless, in recent years, an increasing number of bridging compounds have been reported, which might be traced back to the fact that several of them were prepared by thermal decomposition of precursors that contain terminal anionic ligands (Näther *et al.*, 2013). In this context, we and others have reported on several new thiocyanate coordination polymers based on transition-metal thiocyanates, in which the metal cations are linked by bridging anionic ligands into chains (Rams *et al.*, 2017; Baran *et al.*, 2019; Wöhlert *et al.*, 2013, 2014b; Mautner *et al.*, 2018). Most of these compounds contain $Mn^{II}$, $Fe^{II}$, $Co^{II}$, $Ni^{II}$ or $Cu^{II}$ cations, whereas no bridging compounds are reported with chromium.



Cr, N, C, S, H
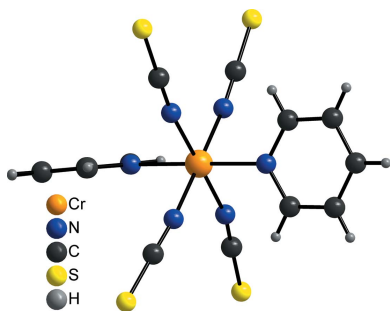
There is only one compound in which alternating Cr$^{III}$ and K$^+$ cations are bridged by $\mu$-1,3-coordinating thiocyanate anions into chains in which each cation is octahedrally sourrounded by two bridging thiocyanate anions and four pyridine ligands (Kitanovski *et al.*, 2007). Therefore, we decided to investigated if similar compounds are available with chromium. Hence, CrCl$_2$ was reacted with NH$_4$NCS to prepare Cr(NCS)$_2$ *in situ*, which is similar to the procedure we frequently use for the synthesis of thiocyanate coordination polymers with other metal cations. Initially, pyridine was selected as the N-donor ligand, because most of our compounds are based on pyridine derivatives as co-ligands. In this reaction, crystals were obtained that were identified by single-crystal X-ray diffraction. This proved that a discrete cationic complex had formed.

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cr1—N2$^i$ | 1.980 (5) | Cr1—N1$^i$ | 1.991 (5) |
| Cr1—N2 | 1.980 (5) | Cr1—N21 | 2.080 (6) |
| Cr1—N1 | 1.991 (5) | Cr1—N11 | 2.102 (6) |
| | | | |
| N2$^i$—Cr1—N2 | 88.4 (3) | N1—Cr1—N21 | 90.39 (18) |
| N2$^i$—Cr1—N1 | 91.33 (18) | N1$^i$—Cr1—N21 | 90.40 (18) |
| N2—Cr1—N1 | 178.9 (2) | N2$^i$—Cr1—N11 | 88.98 (18) |
| N2$^i$—Cr1—N1$^i$ | 178.9 (2) | N2—Cr1—N11 | 88.98 (18) |
| N2—Cr1—N1$^i$ | 91.33 (18) | N1—Cr1—N11 | 90.00 (18) |
| N1—Cr1—N1$^i$ | 88.9 (3) | N1$^i$—Cr1—N11 | 90.00 (18) |
| N2$^i$—Cr1—N21 | 90.62 (18) | N21—Cr1—N11 | 179.4 (3) |
| N2—Cr1—N21 | 90.62 (18) | | |

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

elongation of 1.0015 and the octahedral angle variance of 0.9447° calculated according to Robinson *et al.* (1971). The four isothiocyanate anions are located in the basal plane of the octahedron, whereas the pyridine ligands are in apical positions with the pyridine ring planes rotated by 90° (Fig. 2). Charge balance is achieved by a pyridinium cation that is hydrogen bonded to a pyridine solvent molecule *via* N—H···N hydrogen bonding, forming pyridinium–pyridine dimers (Fig. 3). Several models were tested, but in the final refinement, a split model was used, in which the pyridinium H atom is disordered over two sites in a ratio of 70:30. Presumably, because of sterical reasons, the pyridine-ring planes are perpendicular to each other (Fig. 3).

## 2. Structural commentary

The asymmetric unit of the title compound consists of one half of the cation, namely a Cr$^{III}$ ion, two pyridine ligands which lie on a crystallographic mirror plane and two isothiocyanate anions that occupy general positions, as well as one pyridinium cation and a pyridine molecule that are also located on a crystallographic mirror plane (Fig. 1). The Cr$^{III}$ ion is sixfold coordinated by four *N*-bonding isothiocyanate anions and two pyridine ligands, within a slightly distorted octahedral geometry (Figs. 1 and 2). The Cr—N bond lengths (Table 1) to the pyridine ligands (N11 and N21) are slightly longer than that to the isothiocyanate anions (N1 and N2). The distortion of the octahedron is also obvious from the mean quadratic
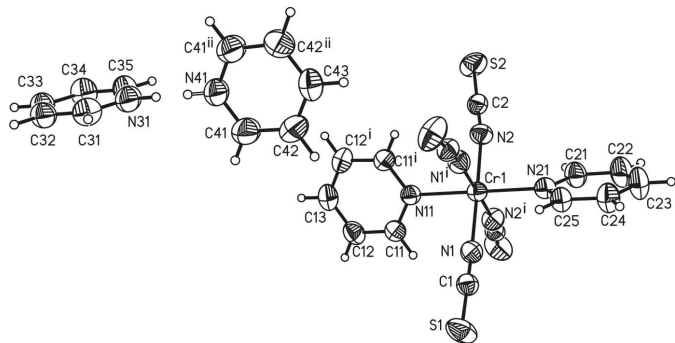
**Figure 3**
View of the pyridinium–pyridine dimer, with N–H···N hydrogen bonding shown as dashed lines. The pyridinium N-bound H atom is disordered over two sets of sites.

**Figure 1**
The molecular structure of the title compound with the atom labelling and displacement ellipsoids drawn at the 50% probability level. The pyridinium N-bound H atom is disordered over two sets of sites.
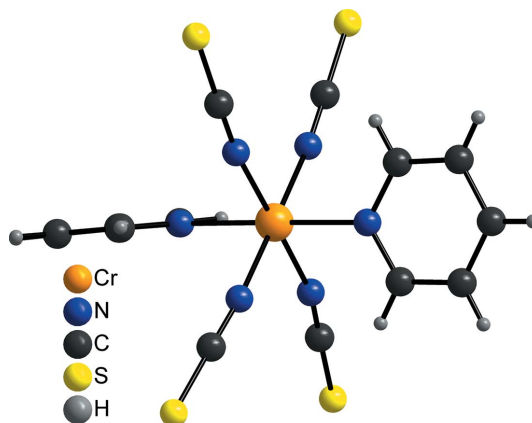
**Figure 2**
View of the coordination sphere of the Cr$^{III}$ ion.

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C12—H12$\cdots$S1$^{ii}$ | 0.93 | 2.93 | 3.647 (6) | 135 |
| C32—H32$\cdots$S2$^{iii}$ | 0.93 | 3.01 | 3.719 (8) | 134 |
| C32—H32$\cdots$S2$^{iv}$ | 0.93 | 3.01 | 3.719 (8) | 134 |
| C35—H35$\cdots$S2$^{v}$ | 0.93 | 2.90 | 3.494 (7) | 123 |
| C35—H35$\cdots$S2$^{vi}$ | 0.93 | 2.90 | 3.494 (7) | 123 |
| N31$A$—H31$A\cdots$N41 | 0.86 | 1.82 | 2.684 (11) | 179 |
| N41$A$—H41$A\cdots$N31 | 0.86 | 1.82 | 2.684 (11) | 180 |

Symmetry codes: (ii) $x, y + 1, z$; (iii) $-x, -y + 2, z - \frac{1}{2}$; (iv) $x, -y + 2, z - \frac{1}{2}$; (v) $x, y, z - 1$; (vi) $-x, y, z - 1$.

## 3. Supramolecular features

In the crystal, discrete complexes and pyridinium cations are arranged in alternating layers parallel to the *bc* plane (Fig. 4, bottom). The discrete complexes are linked by pairs of C—H$\cdots$S hydrogen bonds between the thiocyanate S atoms of one complex and two H atoms of one of the pyridine ligands of a neighbouring complex into chains, that elongate along the crystallographic *b* axis (Fig. 4, top). The bond lengths and angles of these hydrogen bonds show that this is only a very weak interaction (Table 2). These chains are further linked by additional very weak C—H$\cdots$S interactions between the thiocyanate S atoms that are not involved in chain formation
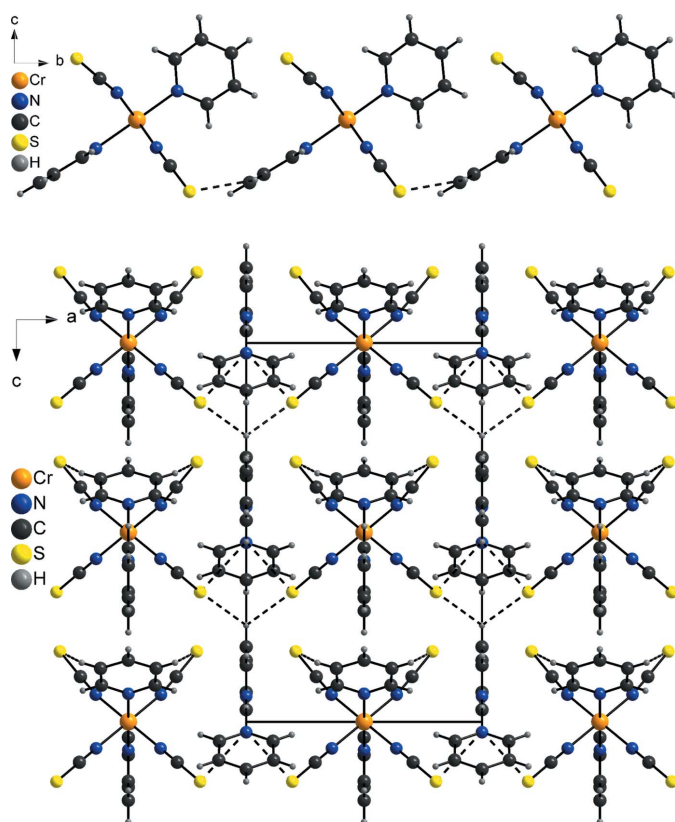


**Figure 4**
View of a chain (top) and the crystal structure of the title compound viewed along the crystallographic *b*-axis and with the intermolecular hydrogen bonding shown as dashed lines.

and one H atom of the pyridinium–pyridine dimers (Fig. 4, bottom, and Table 2). Finally, further C—H$\cdots$S interactions link all building blocks into a three-dimensional network. It is noted that both the discrete complexes, as well as the pyridinium–pyridine dimers, point in the same direction along the crystallographic *c* axis, clearly showing the presence of a polar structure (Fig. 4, bottom).

## 4. Database survey

There are four structures published in the CSD (Version 5.4, Update 1, February 2019; Groom *et al.*, 2016) that consist of chromium(II) and thiocyanate anions. In all of them, the Cr$^{II}$ cations are square-planar coordinated by two isothiocyanate anions and two co-ligands (Jubb *et al.*, 1989, 1991; Shurdha *et al.*, 2012, 2013). With chromium(III) there are two structures in which the cations are octahedrally coordinated by only two terminal isothiocyanate anions and by two 4,4′-dimethyl-2,2′-pyridine ligands and the positive charge is neutralized by iodide or triiodide anions (Walter & Elliott, 2001). In most of the reported structures with Cr$^{III}$, the cations are surrounded by four or six isothiocyanate anions and the positive charges are neutralized by protonated solvent or ligand molecules. There is also one discrete complex with pyridine as co-ligand, in which the Cr$^{III}$ cations are coordinated by three isothiocyanate anions and three pyridine ligands (Malecki, 2016). A similar structure is also known with 4-methylpyridine (Kitanovski *et al.*, 2007). Finally, there is one structure reported that is comparable to that of the title compound with 4-methylpyridine, in which the Cr$^{III}$ cations are coordinated by two 4-methylpyridine ligands and four *N*-terminal thiocyanate anions. Charge balance is achieved by one 4-methylpyridinium cation that is hydrogen bonded to one 4-methylpyridine solvent molecule (Young *et al.*, 2011). In contrast to the title compound, the N—H distances are not symmetrical (N—H = 1.16 Å and N$\cdots$H = 1.5 Å), but the N—H$\cdots$N hydrogen-bond distance is comparable (2.686 Å) to that in the title compound (2.684 Å).

## 5. Synthesis and crystallization

CrCl$_2$ (0.5 mmol, 66.5 mg) was reacted with NH$_4$NCS (1.0 mmol, 76.1 mg) in 2.0 ml pyridine. The precipitate was filtered off and the filtrate was stored at room temperature. After a few days, crystals of the title compound suitable for single-crystal x-ray diffraction were obtained.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms were positioned with idealized geometry and refined with $U_{iso}(H) = 1.2U_{eq}(C)$ using a riding model. The pyridinium H atom was located in a difference map and was initially freely refined. In this case, it is located nearly in the middle between both pyridine N atoms, leading to very long N—H bonds of 1.32 (16) and 1.35 (16) Å, an N—H$\cdots$N angle close to linearity and a relatively large

isotropic displacement parameter. For such N—H$\cdots$N hydrogen bonds, both symmetric and asymmetric hydrogen bonds were determined by neutron diffraction, but the symmetric bonds are usually observed at shorter N$\cdots$N distances (Rozière *et al.*, 1980, 1982). Therefore, the pyridinium H atom was placed at an ideal distance and the displacement parameter was refined. In this case, there is a strong indication that the H atom is disordered and therefore a split model was used with the site-occupation factor for each H atom in a ratio of 70:30, which leads to similar isotropic displacement parameters that are lower than that obtained by the refinement of a symmetrical hydrogen bond. In the final refinement, both H atoms were placed in ideal positions and were refined with $U_{iso}(H) = 1.2U_{eq}(N)$ using a riding model.

## Acknowledgements

## Funding information

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**Table 3**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $(C_5H_6N)[Cr(NCS)_4(C_5H_5N)_2]\cdot C_5H_5N$ |
| $M_r$ | 601.73 |
| Crystal system, space group | Orthorhombic, $Pmc2_1$ |
| Temperature (K) | 293 |
| $a, b, c$ (Å) | 10.1068 (5), 8.8168 (6), 16.2628 (9) |
| $V$ (Å$^3$) | 1449.17 (15) |
| $Z$ | 2 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.71 |
| Crystal size (mm) | $0.12 \times 0.07 \times 0.02$ |
| | |
| Data collection | |
| Diffractometer | Stoe IPDS1 |
| Absorption correction | Numerical (*X-SHAPE* and *X-RED32*; Stoe & Cie, 2008) |
| $T_{min}, T_{max}$ | 0.786, 0.966 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 12253, 3153, 2452 |
| $R_{int}$ | 0.062 |
| $(\sin\theta/\lambda)_{max}$ (Å$^{-1}$) | 0.639 |
| | |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.043, 0.106, 1.02 |
| No. of reflections | 3153 |
| No. of parameters | 193 |
| No. of restraints | 1 |
| H-atom treatment | H-atom parameters constrained |
| $\Delta\rho_{max}, \Delta\rho_{min}$ (e Å$^{-3}$) | 0.30, −0.42 |
| Absolute structure | Flack $x$ determined using 925 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013) |
| Absolute structure parameter | −0.027 (19) |

Computer programs: *X-AREA* (Stoe & Cie, 2008), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *XP* in *SHELXTL* (Sheldrick, 2008), *DIAMOND* (Brandenburg, 1999) and *publCIF* (Westrip, 2010).

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# supporting information

## Crystal structure of pyridinium tetraisothiocyanatodipyridinechromium(III) pyridine monosolvate

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**Computing details**

Data collection: *X-AREA* (Stoe & Cie, 2008); cell refinement: *X-AREA* (Stoe & Cie, 2008); data reduction: *X-AREA* (Stoe & Cie, 2008); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

**Pyridinium tetraisothiocyanatobis(pyridine)chromium(III) pyridine monosolvate**

*Crystal data*

| | |
|---|---|
| $(C_5H_6N)[Cr(NCS)_4(C_5H_5N)_2]\cdot C_5H_5N$ | $D_x = 1.379$ Mg m$^{-3}$ |
| $M_r = 601.73$ | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |
| Orthorhombic, $Pmc2_1$ | Cell parameters from 12253 reflections |
| $a = 10.1068$ (5) Å | $\theta = 2.6$–28.1° |
| $b = 8.8168$ (6) Å | $\mu = 0.71$ mm$^{-1}$ |
| $c = 16.2628$ (9) Å | $T = 293$ K |
| $V = 1449.17$ (15) Å$^3$ | Plate, green |
| $Z = 2$ | $0.12 \times 0.07 \times 0.02$ mm |
| $F(000) = 618$ | |

*Data collection*

| | |
|---|---|
| Stoe IPDS1 diffractometer | 3153 independent reflections |
| | 2452 reflections with $I > 2\sigma(I)$ |
| Phi scans | $R_{int} = 0.062$ |
| Absorption correction: numerical (X-SHAPE and X-RED32; Stoe & Cie, 2008) | $\theta_{max} = 27.0°$, $\theta_{min} = 2.6°$ |
| | $h = -11 \rightarrow 12$ |
| $T_{min} = 0.786$, $T_{max} = 0.966$ | $k = -11 \rightarrow 11$ |
| 12253 measured reflections | $l = -20 \rightarrow 20$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | H-atom parameters constrained |
| Least-squares matrix: full | $w = 1/[\sigma^2(F_o^2) + (0.0503P)^2 + 0.4808P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $R[F^2 > 2\sigma(F^2)] = 0.043$ | |
| $wR(F^2) = 0.106$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.02$ | $\Delta\rho_{max} = 0.30$ e Å$^{-3}$ |
| 3153 reflections | $\Delta\rho_{min} = -0.42$ e Å$^{-3}$ |
| 193 parameters | Absolute structure: Flack $x$ determined using 925 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons *et al.*, 2013) |
| 1 restraint | |
| Hydrogen site location: inferred from neighbouring sites | Absolute structure parameter: −0.027 (19) |

*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 (Å²)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ | Occ. (<1) |
|---|---|---|---|---|---|
| Cr1 | 0.500000 | 0.64497 (13) | 0.99944 (7) | 0.0350 (3) | |
| N1 | 0.6380 (5) | 0.5526 (5) | 0.9278 (3) | 0.0456 (11) | |
| C1 | 0.7030 (6) | 0.4870 (6) | 0.8803 (3) | 0.0409 (12) | |
| S1 | 0.7901 (2) | 0.39515 (18) | 0.81396 (11) | 0.0671 (5) | |
| N2 | 0.3635 (5) | 0.7405 (5) | 1.0697 (3) | 0.0453 (11) | |
| C2 | 0.2924 (6) | 0.8219 (6) | 1.1063 (3) | 0.0410 (12) | |
| S2 | 0.1955 (2) | 0.9312 (2) | 1.15735 (11) | 0.0689 (5) | |
| N11 | 0.500000 | 0.8403 (7) | 0.9254 (4) | 0.0378 (13) | |
| C11 | 0.6137 (6) | 0.9059 (6) | 0.9028 (3) | 0.0446 (13) | |
| H11 | 0.693081 | 0.859637 | 0.917262 | 0.053* | |
| C12 | 0.6175 (7) | 1.0412 (6) | 0.8584 (4) | 0.0522 (14) | |
| H12 | 0.697858 | 1.084674 | 0.843515 | 0.063* | |
| C13 | 0.500000 | 1.1087 (10) | 0.8372 (5) | 0.054 (2) | |
| H13 | 0.499999 | 1.200033 | 0.808600 | 0.065* | |
| N21 | 0.500000 | 0.4529 (7) | 1.0738 (4) | 0.0380 (14) | |
| C21 | 0.500000 | 0.4633 (10) | 1.1565 (5) | 0.051 (2) | |
| H21 | 0.500000 | 0.558953 | 1.180637 | 0.061* | |
| C22 | 0.500000 | 0.3371 (11) | 1.2067 (6) | 0.065 (3) | |
| H22 | 0.500000 | 0.348073 | 1.263584 | 0.078* | |
| C23 | 0.500000 | 0.1953 (12) | 1.1719 (6) | 0.068 (3) | |
| H23 | 0.500000 | 0.109435 | 1.205088 | 0.082* | |
| C24 | 0.500000 | 0.1805 (10) | 1.0868 (6) | 0.059 (2) | |
| H24 | 0.500000 | 0.085445 | 1.061946 | 0.070* | |
| C25 | 0.500000 | 0.3110 (9) | 1.0405 (5) | 0.0441 (18) | |
| H25 | 0.500000 | 0.301981 | 0.983543 | 0.053* | |
| N31 | 0.000000 | 1.0017 (9) | 0.4322 (5) | 0.061 (2) | |
| H31A | 0.000000 | 0.920955 | 0.461881 | 0.073* | 0.3 |
| C31 | 0.000000 | 0.9933 (10) | 0.3502 (6) | 0.057 (2) | |
| H31 | 0.000000 | 0.898380 | 0.325264 | 0.068* | |
| C32 | 0.000000 | 1.1428 (12) | 0.4678 (6) | 0.062 (2) | |
| H32 | 0.000000 | 1.150849 | 0.524812 | 0.075* | |
| C33 | 0.000000 | 1.2701 (11) | 0.4217 (6) | 0.060 (2) | |
| H33 | 0.000000 | 1.364655 | 0.447130 | 0.072* | |
| C34 | 0.000000 | 1.2604 (10) | 0.3374 (5) | 0.051 (2) | |
| H34 | 0.000000 | 1.347438 | 0.305068 | 0.061* | |
| C35 | 0.000000 | 1.1195 (10) | 0.3021 (5) | 0.051 (2) | |
| H35 | 0.000000 | 1.109984 | 0.245176 | 0.062* | |
| N41 | 0.000000 | 0.7526 (8) | 0.5271 (5) | 0.0557 (19) | |
| H41A | 0.000000 | 0.832178 | 0.496530 | 0.067* | 0.7 |

| | | | |
|---|---|---|---|
| C41 | 0.1138 (8) | 0.6919 (8) | 0.5505 (5) | 0.0686 (19) |
| H41 | 0.192859 | 0.735531 | 0.533295 | 0.082* |
| C42 | 0.1165 (8) | 0.5636 (8) | 0.6004 (5) | 0.071 (2) |
| H42 | 0.196943 | 0.522486 | 0.617040 | 0.085* |
| C43 | 0.000000 | 0.4985 (10) | 0.6248 (5) | 0.057 (2) |
| H43 | 0.000001 | 0.411685 | 0.657268 | 0.069* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cr1 | 0.0346 (6) | 0.0369 (5) | 0.0333 (5) | 0.000 | 0.000 | −0.0032 (5) |
| N1 | 0.048 (3) | 0.049 (3) | 0.039 (2) | 0.001 (2) | 0.000 (2) | 0.001 (2) |
| C1 | 0.040 (3) | 0.037 (3) | 0.045 (3) | −0.001 (2) | 0.006 (3) | −0.001 (2) |
| S1 | 0.0761 (13) | 0.0503 (8) | 0.0749 (11) | −0.0015 (8) | 0.0372 (9) | −0.0093 (8) |
| N2 | 0.045 (3) | 0.047 (3) | 0.044 (3) | 0.002 (2) | 0.006 (2) | −0.003 (2) |
| C2 | 0.040 (3) | 0.045 (3) | 0.038 (3) | 0.001 (2) | −0.003 (2) | 0.001 (2) |
| S2 | 0.0684 (12) | 0.0846 (12) | 0.0537 (9) | 0.0326 (9) | 0.0046 (9) | −0.0143 (8) |
| N11 | 0.036 (4) | 0.040 (3) | 0.037 (3) | 0.000 | 0.000 | −0.001 (3) |
| C11 | 0.041 (3) | 0.046 (3) | 0.047 (3) | −0.003 (2) | 0.001 (2) | 0.004 (2) |
| C12 | 0.059 (4) | 0.045 (3) | 0.052 (3) | −0.007 (3) | 0.010 (3) | 0.005 (3) |
| C13 | 0.071 (6) | 0.045 (4) | 0.046 (5) | 0.000 | 0.000 | 0.006 (4) |
| N21 | 0.040 (4) | 0.035 (3) | 0.039 (3) | 0.000 | 0.000 | −0.004 (2) |
| C21 | 0.064 (6) | 0.054 (5) | 0.035 (4) | 0.000 | 0.000 | −0.001 (3) |
| C22 | 0.090 (8) | 0.064 (6) | 0.042 (4) | 0.000 | 0.000 | 0.007 (4) |
| C23 | 0.096 (8) | 0.059 (6) | 0.050 (5) | 0.000 | 0.000 | 0.022 (5) |
| C24 | 0.074 (7) | 0.047 (5) | 0.055 (5) | 0.000 | 0.000 | 0.007 (4) |
| C25 | 0.051 (5) | 0.042 (4) | 0.039 (4) | 0.000 | 0.000 | 0.001 (3) |
| N31 | 0.051 (5) | 0.055 (4) | 0.075 (5) | 0.000 | 0.000 | 0.020 (4) |
| C31 | 0.059 (6) | 0.045 (4) | 0.066 (6) | 0.000 | 0.000 | −0.005 (4) |
| C32 | 0.066 (6) | 0.076 (6) | 0.045 (4) | 0.000 | 0.000 | 0.003 (5) |
| C33 | 0.073 (7) | 0.051 (5) | 0.055 (5) | 0.000 | 0.000 | −0.010 (4) |
| C34 | 0.054 (5) | 0.053 (5) | 0.045 (4) | 0.000 | 0.000 | −0.001 (4) |
| C35 | 0.052 (5) | 0.059 (5) | 0.043 (4) | 0.000 | 0.000 | −0.009 (4) |
| N41 | 0.054 (5) | 0.050 (4) | 0.063 (5) | 0.000 | 0.000 | 0.014 (3) |
| C41 | 0.051 (4) | 0.064 (4) | 0.091 (5) | 0.000 (3) | 0.004 (4) | 0.017 (4) |
| C42 | 0.056 (5) | 0.071 (4) | 0.086 (5) | 0.016 (3) | −0.002 (4) | 0.018 (4) |
| C43 | 0.079 (7) | 0.045 (4) | 0.047 (5) | 0.000 | 0.000 | 0.009 (4) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cr1—N2$^i$ | 1.980 (5) | C23—H23 | 0.9300 |
| Cr1—N2 | 1.980 (5) | C24—C25 | 1.375 (11) |
| Cr1—N1 | 1.991 (5) | C24—H24 | 0.9300 |
| Cr1—N1$^i$ | 1.991 (5) | C25—H25 | 0.9300 |
| Cr1—N21 | 2.080 (6) | N31—C31 | 1.336 (13) |
| Cr1—N11 | 2.102 (6) | N31—C32 | 1.372 (13) |
| N1—C1 | 1.168 (7) | N31—H31A | 0.8600 |
| C1—S1 | 1.610 (6) | C31—C35 | 1.360 (13) |

| | | | |
|---|---|---|---|
| N2—C2 | 1.177 (7) | C31—H31 | 0.9300 |
| C2—S2 | 1.605 (6) | C32—C33 | 1.350 (13) |
| N11—C11 | 1.338 (7) | C32—H32 | 0.9300 |
| N11—C11i | 1.338 (7) | C33—C34 | 1.375 (12) |
| C11—C12 | 1.395 (7) | C33—H33 | 0.9300 |
| C11—H11 | 0.9300 | C34—C35 | 1.368 (11) |
| C12—C13 | 1.373 (8) | C34—H34 | 0.9300 |
| C12—H12 | 0.9300 | C35—H35 | 0.9300 |
| C13—H13 | 0.9300 | N41—C41 | 1.324 (8) |
| N21—C21 | 1.349 (10) | N41—C41ii | 1.324 (8) |
| N21—C25 | 1.363 (10) | N41—H41A | 0.8600 |
| C21—C22 | 1.379 (12) | C41—C42 | 1.393 (9) |
| C21—H21 | 0.9300 | C41—H41 | 0.9300 |
| C22—C23 | 1.373 (15) | C42—C43 | 1.369 (9) |
| C22—H22 | 0.9300 | C42—H42 | 0.9300 |
| C23—C24 | 1.390 (13) | C43—H43 | 0.9300 |
| | | | |
| N2i—Cr1—N2 | 88.4 (3) | C22—C23—C24 | 119.8 (9) |
| N2i—Cr1—N1 | 91.33 (18) | C22—C23—H23 | 120.1 |
| N2—Cr1—N1 | 178.9 (2) | C24—C23—H23 | 120.1 |
| N2i—Cr1—N1i | 178.9 (2) | C25—C24—C23 | 117.8 (9) |
| N2—Cr1—N1i | 91.33 (18) | C25—C24—H24 | 121.1 |
| N1—Cr1—N1i | 88.9 (3) | C23—C24—H24 | 121.1 |
| N2i—Cr1—N21 | 90.62 (18) | N21—C25—C24 | 123.5 (7) |
| N2—Cr1—N21 | 90.62 (18) | N21—C25—H25 | 118.3 |
| N1—Cr1—N21 | 90.39 (18) | C24—C25—H25 | 118.3 |
| N1i—Cr1—N21 | 90.40 (18) | C31—N31—C32 | 118.1 (8) |
| N2i—Cr1—N11 | 88.98 (18) | C31—N31—H31A | 120.9 |
| N2—Cr1—N11 | 88.98 (18) | C32—N31—H31A | 120.9 |
| N1—Cr1—N11 | 90.00 (18) | N31—C31—C35 | 121.9 (8) |
| N1i—Cr1—N11 | 90.00 (18) | N31—C31—H31 | 119.0 |
| N21—Cr1—N11 | 179.4 (3) | C35—C31—H31 | 119.0 |
| C1—N1—Cr1 | 169.7 (5) | C33—C32—N31 | 121.4 (9) |
| N1—C1—S1 | 178.9 (6) | C33—C32—H32 | 119.3 |
| C2—N2—Cr1 | 167.6 (5) | N31—C32—H32 | 119.3 |
| N2—C2—S2 | 179.1 (5) | C32—C33—C34 | 120.1 (9) |
| C11—N11—C11i | 118.4 (7) | C32—C33—H33 | 119.9 |
| C11—N11—Cr1 | 120.8 (3) | C34—C33—H33 | 119.9 |
| C11i—N11—Cr1 | 120.7 (3) | C35—C34—C33 | 118.3 (8) |
| N11—C11—C12 | 122.4 (6) | C35—C34—H34 | 120.8 |
| N11—C11—H11 | 118.8 | C33—C34—H34 | 120.8 |
| C12—C11—H11 | 118.8 | C31—C35—C34 | 120.1 (8) |
| C13—C12—C11 | 118.5 (6) | C31—C35—H35 | 119.9 |
| C13—C12—H12 | 120.8 | C34—C35—H35 | 119.9 |
| C11—C12—H12 | 120.8 | C41—N41—C41ii | 120.6 (8) |
| C12i—C13—C12 | 119.8 (8) | C41—N41—H41A | 119.7 |
| C12i—C13—H13 | 120.1 | C41ii—N41—H41A | 119.7 |
| C12—C13—H13 | 120.1 | N41—C41—C42 | 120.9 (7) |

| | | | |
|---|---|---|---|
| C21—N21—C25 | 117.3 (7) | N41—C41—H41 | 119.6 |
| C21—N21—Cr1 | 121.6 (5) | C42—C41—H41 | 119.6 |
| C25—N21—Cr1 | 121.1 (5) | C43—C42—C41 | 119.5 (7) |
| N21—C21—C22 | 122.4 (8) | C43—C42—H42 | 120.3 |
| N21—C21—H21 | 118.8 | C41—C42—H42 | 120.3 |
| C22—C21—H21 | 118.8 | C42—C43—C42$^{ii}$ | 118.7 (8) |
| C23—C22—C21 | 119.4 (8) | C42—C43—H43 | 120.6 |
| C23—C22—H22 | 120.3 | C42$^{ii}$—C43—H43 | 120.6 |
| C21—C22—H22 | 120.3 | | |

Symmetry codes: (i) −*x*+1, *y*, *z*; (ii) −*x*, *y*, *z*.

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C12—H12···S1$^{iii}$ | 0.93 | 2.93 | 3.647 (6) | 135 |
| C32—H32···S2$^{iv}$ | 0.93 | 3.01 | 3.719 (8) | 134 |
| C32—H32···S2$^{v}$ | 0.93 | 3.01 | 3.719 (8) | 134 |
| C35—H35···S2$^{vi}$ | 0.93 | 2.90 | 3.494 (7) | 123 |
| C35—H35···S2$^{vii}$ | 0.93 | 2.90 | 3.494 (7) | 123 |
| N31—H31*A*···N41 | 0.86 | 1.82 | 2.684 (11) | 179 |
| N41—H41*A*···N31 | 0.86 | 1.82 | 2.684 (11) | 180 |

Symmetry codes: (iii) *x*, *y*+1, *z*; (iv) −*x*, −*y*+2, *z*−1/2; (v) *x*, −*y*+2, *z*−1/2; (vi) *x*, *y*, *z*−1; (vii) −*x*, *y*, *z*−1.