Isolation and structural comparison of Ru\textsuperscript{II}-dnp complexes [dnp = 2,6-bis(1,8-naphthyridin-2-yl)-pyridine] with axially or equatorially coordinating NCS ligands

Tsugiko Takase,\textsuperscript{a,*} Takashi Yamanaka,\textsuperscript{b} Chihiro Tamura\textsuperscript{b} and Dai Oyama\textsuperscript{a}

\textsuperscript{a}Department of Natural Sciences and Informatics, Fukushima University, 1, Kanayagawa, Fukushima 960-1296, Japan, and \textsuperscript{b}Graduate School of Science and Engineering, Fukushima University, 1 Kanayagawa, Fukushima 960-1296, Japan.

*Correspondence e-mail: ttakase@sss.fukushima-u.ac.jp

The molecular and crystal structures of two ruthenium(II) complexes, viz. \textit{cis}-aqua[2,6-bis(1,8-naphthyridin-2-yl)pyridine-\(\kappa\text{N,N',N''}\)](thiocyanato-\(\kappa\text{N}\))(triphenylphosphine-\(\kappa\text{P}\))ruthenium(II) hexafluoridophosphate–acetone–water (1/0.5/1), [Ru(NCS)(C\textsubscript{21}H\textsubscript{13}N\textsubscript{5})(C\textsubscript{18}H\textsubscript{15}P)(H\textsubscript{2}O)]PF\textsubscript{6}.0.5C\textsubscript{3}H\textsubscript{6}O.H\textsubscript{2}O (I) and \textit{trans}-[2,6-bis(1,8-naphthyridin-2-yl)pyridine-\(\kappa\text{N,N',N''}\)]bis(pyridine-\(\kappa\text{N}\))(thiocyanato-\(\kappa\text{N}\))ruthenium(II) thiocyanate, [Ru(NCS)(C\textsubscript{21}H\textsubscript{13}N\textsubscript{5})(C\textsubscript{5}H\textsubscript{5}N)\textsubscript{2}]NCS (II), with an N-coordinating thiocyanato group and a tridentate polypyridyl supporting ligand, are reported. The Ru\textsuperscript{II} atom in each of the cationic complexes adopts a distorted octahedral coordination sphere, defined by an N atom of the thiocyanato ligand, three N atoms from the tridentate polypyridyl ligand, and an O and P atom in (I) or two pyridine-N atoms in (II) derived from monodentate ligands. The thiocyanato ligand in (I) coordinates in an axial manner to the \{Ru-dnp\} unit [dnp = 2,6-bis(1,8-naphthyridin-2-yl)pyridine], whereas it coordinates in an equatorial manner in (II). In the crystal structure of compound (I), intramolecular C—H⋯O, C—H⋯N and O—H⋯N hydrogen bonds as well as π–π contacts are present, in addition to intermolecular C—H⋯F, C—H⋯O and O—H⋯O hydrogen bonds. In the crystal structure of compound (II), intramolecular C—H⋯N hydrogen bonds are observed along with intermolecular C—H⋯N and C—H⋯S hydrogen bonds as well as a π–π interaction.

1. Chemical context

Polypyridylruthenium(II) complexes play essential roles in key technologies, such as solar energy conversion (Lewis, 2007). In particular, Ru\textsuperscript{II} complexes with thiocyanate ion(s) are interesting as dye molecules for dye-sensitized solar cells (Hagfeldt et al., 2010). As a ligand, the thiocyanate group can bond to metals through the terminal nitrogen or sulfur atoms since it is ambidentate. Linkage isomeric pairs can be distinguished using spectroscopic techniques when they exist as a mixture (Brewster et al., 2011; Vandenburgh et al., 2008). However, identifying the coordinating atom (N or S) by structural analysis is more reliable when only one isomer exists.

A series of Ru\textsuperscript{II} complexes containing a supporting ligand, dnp [dnp = 2,6-bis(1,8-naphthyridin-2-yl)pyridine], were synthesized to extend the π-conjugated system of the terpyridine framework (which is a typical tridentate polypyridyl ligand) and their properties and reactivities reported (Oyama et al., 2013, 2017). In particular, some reactivities such as
ligand substitutions are significantly different in an identical coordination framework when the axial ligands are triphenylphosphine (PPh₃) or pyridine (py) (Oyama et al., 2013, 2017).

During the current study, the reaction of precursors with different axially bound ligands with the NCS⁻ ion resulted in the formation of the cationic complexes cis-(PPh₃,H₂O)-[Ru(dnp)(PPh₃)(NCS⁻/C₉N)(H₂O)]⁺ [(I) as the water/acetone (1/0.5) solvated PF₆⁻ salt] with an axially bound NCS⁻ ligand and trans(py)-[Ru(dnp)(py)₂(NCS⁻/C₉N)]⁺ [(II) as the NCS⁻ salt] with an equatorially bound NCS⁻ ligand. Their crystal structures are reported and compared in this communication.

2. Structural commentary

Figs. 1 and 2 present the molecular structures of compounds (I) and (II), respectively. The Ru⁹⁺ atoms in (I) and (II) exhibit distorted octahedral coordination environments, similar to those reported in other structurally related complexes containing the tridentate dnp ligand (Koizumi & Tanaka, 2005; Oyama et al., 2013, 2017). As listed in Tables 1 and 2, compounds (I) and (II) exhibit intramolecular hydrogen bonds between aromatic C—H groups of PPh₃ or pyridine and the non-coordinating N atoms in dnp or the monodentate ligands [OH₂ in (I) or NCS⁻ in (II)]. In (I), the interatomic distances between O₁ and N₁ [2.678 (4) Å] and O₁ and N₅ [2.983 (4) Å] are considerably short. Although the H atoms of the coordinating water molecule (O₁) have not been localized, these short distances indicate that intramolecular hydrogen bonds of medium strength are present between the aqua ligand and the N atoms of the dnp ligand. Furthermore, in (I) intramolecular π–π interactions [Cg₁···Cg₂ = 3.640 (4) Å and Cg₃···Cg₄ = 3.749 (3) Å where Cg₁, Cg₂, Cg₃, and Cg₄ are the centroids of the N₁/C₁–C₅, C₂₉–C₃₄, N₃/C₉–C₁₃, and C₃₅–

![Figure 1](image1.png)

**Figure 1**
Molecular structure of the complex cation in (I), with atom labels and displacement ellipsoids for non-H atoms drawn at the 50% probability level.

![Figure 2](image2.png)

**Figure 2**
Molecular structure of the complex cation in (II), with atom labels and displacement ellipsoids for non-H atoms drawn at the 50% probability level.

| Compound | D—H···A | D—H | H···A | D···A | D—H···A |
|----------|---------|------|-------|-------|---------|
| (I)      |         |      |       |       |         |
| C₁₀—H₆···F₅¹ | 0.93 | 2.45 | 3.369 (6) | 170 |
| C₁₅—H₉···F₂ | 0.93 | 2.45 | 3.345 (6) | 162 |
| C₂₁—H₁₃···O₂ | 0.93 | 2.59 | 3.213 (14) | 124 |
| C₂₄—H₁₄···O₁ | 0.93 | 2.43 | 3.210 (5) | 141 |
| C₂₄—H₁₄···N₅ | 0.93 | 2.43 | 3.144 (6) | 134 |
| C₂₅—H₁₅···F₄¹ | 0.93 | 2.54 | 3.347 (7) | 145 |
| C₄₁—H₃₀···F₁¹ | 0.96 | 2.40 | 3.26 (3) | 150 |

| Compound | D—H···A | D—H | H···A | D···A | D—H···A |
|----------|---------|------|-------|-------|---------|
| (II)     |         |      |       |       |         |
| C₁₂—H₈···N₀¹ | 0.95 | 2.43 | 3.305 (5) | 152 |
| C₂₀—H₁₂···S₂² | 0.95 | 2.73 | 3.629 (3) | 159 |
| C₂₂—H₁₄···N₁ | 0.95 | 2.51 | 3.391 (3) | 154 |
| C₂₇—H₁₉···S₂ | 0.95 | 2.76 | 3.479 (3) | 133 |

Symmetry codes: (i) −x, −y, −z + 2; (ii) −x + 1, −y + 1, −z + 2.
As mentioned above, it is important to distinguish the coordination atom of the thiocyanato ligand because of its ambidentate coordination mode. Both S- and N-coordinated coordination atom of the thiocyanato ligand because of its overwhelming dominant. These complexes can be distinguished crystallographically by the Ru—X—C bond angle (X = N or S) through the coordinating atom. For example, the Ru—S—C bond angles (for S-ligating examples) are in the range 159–179° whereas the Ru—N—C bond angles (for N-ligating examples) are 104–106°. 

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The bond length between the RuII atom and the nitrogen atom in (I) [2.105 (3) Å] is slightly longer than that of (II) [2.069 (2) Å]. In contrast, the N≡C bond length in (I) [1.116 (5) Å] is shorter than that of (II) [1.160 (3) Å]. The terminal C—S distance [(I): 1.637 (4) Å, (II): 1.647 (2) Å] and the N—C—S bond angle [(I): 178.2 (4)°, (II): 179.0 (2)°] are similar. These data are in agreement with those of the related polypyridyl complexes containing N-bound {RuII–NCS}⁺ moieties (Brewster et al., 2011; Cadranel et al., 2012; Shklover et al., 2002; Vandeburgh et al., 2008; Zakeeruddin et al., 1997).

### 3. Supramolecular features

Additional solvent molecules are incorporated in the crystal structure of (I), i.e., a water molecule and a disordered acetone molecule (occupancy 0.5) per formula unit. Apart from Coulombic forces, there are weak C—H···F hydrogen bonds between the complex cation and the PF₆⁻ anion (Table 1) and the acetone molecule [O1···O2 = 2.87 (1) Å]. These interactions contribute to the stabilization of the packing and formation of a three-dimensional supramolecular structure (Fig. 3).

In the crystal structure of (II), weak C—H···X (X = N or S) hydrogen-bonding interactions exist between the complex cation and the NCS⁻ anion (Table 2) along with the intramolecular hydrogen bonds. Additional π···π interactions [Cg5···Cg5’ = 4.0093 (15) Å; Cg5 is the centroid of the N5/C17–C21 ring; symmetry code: (i) 1 − x, 1 − y, 1 − z] with a centroid slippage of 1.263 Å for Cg5···Cg5’ are present. The slippage angle β is 18.4° for Cg5···Cg5’. These interactions lead to the formation of a three-dimensional network structure (Fig. 4).

### 4. Database survey

Some crystal structures of RuII complexes with both N-coordinating thiocyanato and tridentate terpyridine derivative ligands (tpyR) of the form [Ru(tpyR)(NCS)L₂]²⁺ (R = various substituents, L = pyridyl or NCS ligands) have been reported, as revealed by a search of the Cambridge Crystal Structure Database (CSD, version 5.42, update September 2021; Groom et al., 2016), including refcodes NAMCEL (Brewster et al., 2011), CAQRAP (Cadranel et al., 2012), MIXGOP01 (Shklover et al., 2002), and NUMBOM (Zakeeruddin et al., 1997). In contrast, for NAMCIP (Brewster et al., 2011),


**Table 3**

| (I) | (II) |
| --- | --- |
| Chemical data | [Ru(NCS)(C₂H₃N₃)(C₆H₄P)(H₂O)]PF₆⁻ | [Ru(NCS)(C₂H₃N₃)(C₆H₄N₂)]NCS |
| Chemical formula | 0.5C₆H₄O⁻H₂O | 710.79 |
| Crystal system, space group | Triclinic, P1 | Monoclinic, P2₁/c |
| Temperature (K) | 296 | 93 |
| a, b, c (Å) | 9.3699 (2), 15.3897 (4), 16.0267 (4) | 12.6556 (10), 14.0986 (7), 17.4421 (14) |
| V (Å³) | 2186.29 (10) | 2950.7 (4) |
| Z | 2 | 4 |
| Radiation type | Mo Kα | Mo Kα |
| μ (mm⁻¹) | 0.55 | 0.72 |
| Crystal size (mm) | 0.20 × 0.15 × 0.10 | 0.25 × 0.15 × 0.05 |

**Data collection**

| (I) | (II) |
| --- | --- |
| Diffractometer | Rigaku R-AXIS RAPID | Rigaku Saturn724 |
| Absorption correction | Multi-scan (ABSCOR; Rigaku, 1995) | Multi-scan (REQAB; Rigaku, 1998) |
| Tmin, Tmax | 0.750, 0.947 | 0.927, 0.965 |
| No. of measured, independent and observed | 34567, 9994, 8406 | 30135, 6758, 6058 |
| F² > 2σ(F²) | 0.025 | 0.029 |
| (sinθ/λ)max (Å⁻¹) | 0.649 | 0.649 |

**Refinement**

| (I) | (II) |
| --- | --- |
| R[F² > 2σ(F²)], wR(F²), S | 0.050, 0.169, 1.08 | 0.036, 0.091, 1.10 |
| No. of reflections | 9994 | 6758 |
| No. of parameters | 554 | 406 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained |
| Δρmax, Δρmin (e Å⁻³) | 1.93, −0.64 | 1.13, −0.81 |

**Computer programs:** RAPID-AUTO (Rigaku, 2006), CrystalClear (Rigaku, 2015), SIR97 (Altomare et al., 1999), SIR92 (Altomare et al., 1993), SHELXL2018/3 (Sheldrick, 2015), Mercury (Macrae et al., 2020), ORTEP-3 for Windows (Farrugia, 2012), CrystalStructure (Rigaku, 2019), PLATON (Spek, 2020) and pubICIF (Westrup, 2010).

5. Synthesis and crystallization

A methanolic solution (40 ml) containing [Ru(dnp)(PPh₃)₂(H₂O)]PF₆ (50 mg, 0.039 mmol) (Oyama et al., 2013) and 1.1 eq. of NaSCN (10 mg) was heated under reflux for 30 min. The volume was reduced to 5 ml, and a saturated solution of KPF₆ was added. The resulting solid was filtered and washed sequentially with water and diethyl ether. The yield was 32 mg (69%). Crystals suitable for use in X-ray diffraction (XRD) studies were grown by vapor diffusion of diethyl ether into an acetonitrile solution of (I). Fourier transform infrared (FTIR) spectroscopy using a KBr pellet showed νCN at 2130 cm⁻¹.

For the synthesis of compound (II), a methanolic solution (20 ml) containing [Ru(dnp)(py)₂(H₂O)]PF₆ (25 mg, 0.028 mmol) (Oyama et al., 2013) and 2.2 eq. of NaSCN (5 mg) was heated under reflux for 30 min. The reaction mixture was reduced to 3 ml. The addition of diethyl ether (5 ml) to the solution resulted in the formation of a precipitate of (II). The crude product was purified by column chromatography on Al₂O₃ (eluent: acetone). The yield was 9 mg (40%). Single crystals suitable for XRD studies were obtained by recrystallization from acetone. FTIR using a KBr pellet showed νCN at 2121 (ligand) and 2055 cm⁻¹ (counter-ion).

6. Refinement

Table 3 lists the crystal data, data collection, and structure refinement details. All hydrogen atoms were placed at calculated positions [C—H = 0.93 or 0.96 Å in (I), C—H = 0.95 Å in (II)] and refined using a riding model with Uiso(H) = 1.2Ueq(C). The acetone solvent molecule in (I) (C41–C43, O2) is disordered over an inversion center and was refined with an occupancy of 0.5. The oxygen atom of the solvent water molecule (O3) was refined with an isotropic displacement parameter. H atoms of the coordinating and the solvate water molecules could not be localized from difference-Fourier maps. Therefore, they are not part of the model but part of the formula.

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V. & Haibach, T. (1997). *Inorg. Chem.* **36**, 5937–5946.
Isolation and structural comparison of RuII-dnp complexes [dnp = 2,6-bis(1,8-naphthyridin-2-yl)pyridine] with axially or equatorially coordinating NCS ligands

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Computing details
Data collection: RAPID-AUTO (Rigaku, 2006) for (I); CrystalClear (Rigaku, 2015) for (II). Cell refinement: RAPID-AUTO (Rigaku, 2006) for (I); CrystalClear (Rigaku, 2015) for (II). Data reduction: RAPID-AUTO (Rigaku, 2006) for (I); CrystalClear (Rigaku, 2015) for (II). Program(s) used to solve structure: SIR97 (Altomare et al., 1999) for (I); SIR92 (Altomare et al., 1993) for (II). For both structures, program(s) used to refine structure: SHELXL2018/3 (Sheldrick, 2015); molecular graphics: Mercury (Macrae et al., 2020), ORTEP-3 for Windows (Farrugia, 2012); software used to prepare material for publication: CrystalStructure (Rigaku, 2019), PLATON (Spek, 2020) and publCIF (Westrip, 2010).

cis-Aqua[2,6-bis(1,8-naphthyridin-2-yl)pyridine-κ3N,N′,N″](thiocyanato-κN)(triphenylphosphine-κP)ruthenium(II) hexafluoridophosphate–acetone–water (1/0.5/1) (I)

Crystal data
[Ru(NCS)(C21H13N5)(C18H15P)(H2O)]PF6·0.5C3H6O·H2O  
Mr = 966.84  
Triclinic, Pı  
\(a = 9.3699 (2) \text{ Å}\)  
\(b = 15.3897 (4) \text{ Å}\)  
\(c = 16.0267 (4) \text{ Å}\)  
\(α = 92.6869 (9)°\)  
\(β = 105.1544 (8)°\)  
\(γ = 100.0149 (7)°\)  
\(V = 2186.29 (10) \text{ Å}^3\)  
Z = 2  
\(F(000) = 980.00\)  
\(D_x = 1.469 \text{ Mg m}^{-3}\)  
Cell parameters from 29007 reflections  
\(θ = 3.0–27.5°\)  
\(µ = 0.55 \text{ mm}^{-1}\)  
\(T = 296 \text{ K}\)  
Block, purple  
0.20 × 0.15 × 0.10 mm

Data collection
Rigaku R-AXIS RAPID  
diffractometer  
Detector resolution: 10.000 pixels mm\(^{-1}\)  
\(ω\) scans  
Absorption correction: multi-scan  
(ABSCOR; Rigaku, 1995)  
\(T_{\text{min}} = 0.750, T_{\text{max}} = 0.947\)  
34567 measured reflections  
9994 independent reflections  
8406 reflections with \(F^2 > 2.0σ(F^2)\)  
\(R_{\text{int}} = 0.025\)  
\(θ_{\text{max}} = 27.5°, θ_{\text{min}} = 3.0°\)  
\(h = -11→12\)  
\(k = -19→19\)  
\(l = -20→20\)
Refinement

Refinement on $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.050$

$wR(F^2) = 0.169$

$S = 1.08$

9994 reflections

554 parameters

0 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1102P)^2 + 1.1681P]$

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

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

$\Delta \rho_{\text{max}} = 1.93 \text{ e Å}^{-3}$

$\Delta \rho_{\text{min}} = -0.64 \text{ e Å}^{-3}$

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.

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on $F^2$. R-factor (gt) are based on $F$. The threshold expression of $F^2 > 2.0 \sigma(F^2)$ is used only for calculating R-factor (gt).

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{Å}^2$)

| x   | y    | z    | $U_{eq}^*$/$U_{eq}$ | Occ. (<1) |
|-----|------|------|---------------------|-----------|
| Ru1 | 0.20144 (3) | 0.23092 (2) | 0.71810 (2) | 0.03823 (11) |
| S1  | 0.54439 (14) | 0.03779 (10) | 0.68390 (13) | 0.0978 (5) |
| P1  | 0.02612 (10) | 0.31990 (6) | 0.72697 (6) | 0.0440 (2) |
| P2  | 0.28893 (14) | 0.24126 (7) | 1.22614 (7) | 0.0588 (3) |
| F1  | 0.3298 (6) | 0.3196 (2) | 1.3006 (2) | 0.1247 (15) |
| F2  | 0.2484 (4) | 0.16220 (19) | 1.15150 (19) | 0.0894 (9) |
| F3  | 0.2730 (5) | 0.3108 (2) | 1.1558 (2) | 0.1043 (11) |
| F4  | 0.4608 (4) | 0.2498 (3) | 1.2296 (3) | 0.1163 (13) |
| F5  | 0.3020 (4) | 0.1719 (2) | 1.2970 (2) | 0.0948 (10) |
| F6  | 0.1186 (4) | 0.2322 (3) | 1.2222 (3) | 0.1110 (12) |
| O1  | 0.2872 (3) | 0.31914 (19) | 0.63264 (18) | 0.0589 (7) |
| O3  | −0.4347 (17) | 0.1408 (10) | 0.1027 (10) | 0.344 (7)* |
| N1  | 0.0916 (4) | 0.2097 (2) | 0.5019 (2) | 0.0575 (8) |
| N2  | 0.0397 (3) | 0.14350 (19) | 0.62044 (18) | 0.0410 (6) |
| N3  | 0.1213 (3) | 0.3196 (18) | 0.78696 (18) | 0.0415 (6) |
| N4  | 0.3425 (3) | 0.27857 (19) | 0.84298 (19) | 0.0435 (6) |
| N5  | 0.4997 (4) | 0.3928 (2) | 0.8046 (2) | 0.0578 (8) |
| N6  | 0.3590 (3) | 0.1529 (2) | 0.7042 (2) | 0.0508 (7) |
| C1  | 0.0597 (6) | 0.2151 (3) | 0.4174 (3) | 0.0699 (13) |
| H1  | 0.119932 | 0.258875 | 0.396905 | 0.084* |
| C2  | −0.0596 (6) | 0.1587 (3) | 0.3564 (3) | 0.0666 (11) |
| H2  | −0.078108 | 0.297422 | 0.080* |
| C3  | −0.1474 (5) | 0.0940 (3) | 0.3851 (3) | 0.0626 (10) |
| H3  | −0.227518 | 0.346082 | 0.075* |
| C4  | −0.1156 (4) | 0.0850 (3) | 0.4755 (2) | 0.0504 (8) |
| C5  | 0.0039 (4) | 0.1462 (2) | 0.5316 (2) | 0.0462 (7) |
| Atom | X     | Y     | Z     | Uiso  |
|------|-------|-------|-------|-------|
| C6   | -0.1963 (4) | 0.0176 (3) | 0.5117 (3) | 0.0562 (9) |
| H4   | -0.275944 | -0.023686 | 0.476010 | 0.067*  |
| C7   | -0.1565 (4) | 0.0136 (2) | 0.5989 (3) | 0.0505 (8) |
| H5   | -0.207602 | -0.031113 | 0.623294 | 0.061*  |
| C8   | -0.0377 (4) | 0.0773 (2) | 0.6521 (2) | 0.0428 (7) |
| C9   | 0.0081 (4) | 0.0765 (2) | 0.7467 (2) | 0.0459 (7) |
| C10  | -0.0498 (5) | 0.0139 (3) | 0.7941 (3) | 0.0644 (11) |
| H6   | -0.128217 | -0.032599 | 0.766539 | 0.077*  |
| C11  | 0.0111 (6) | 0.0216 (3) | 0.8841 (3) | 0.0817 (16) |
| H7   | -0.026723 | -0.019790 | 0.917268 | 0.098*  |
| C12  | 0.1283 (6) | 0.0913 (3) | 0.9237 (3) | 0.0760 (14) |
| H8   | 0.170109 | 0.096773 | 0.983515 | 0.091*  |
| C13  | 0.1822 (4) | 0.1523 (3) | 0.8740 (2) | 0.0516 (8) |
| C14  | 0.3075 (4) | 0.2288 (3) | 0.9051 (2) | 0.0511 (8) |
| C15  | 0.3825 (5) | 0.2494 (3) | 0.9935 (3) | 0.0679 (12) |
| H9   | 0.354640 | 0.213987 | 1.034253 | 0.081*  |
| C16  | 0.4958 (6) | 0.3212 (3) | 1.0194 (3) | 0.0720 (13) |
| H10  | 0.543541 | 0.336458 | 1.078127 | 0.086*  |
| C17  | 0.5405 (5) | 0.3718 (3) | 0.9579 (3) | 0.0579 (10) |
| C18  | 0.4624 (4) | 0.3486 (2) | 0.8687 (2) | 0.0467 (7) |
| C19  | 0.6592 (6) | 0.4471 (3) | 0.9779 (3) | 0.0787 (14) |
| H11  | 0.713260 | 0.465186 | 1.035344 | 0.094*  |
| C20  | 0.6933 (6) | 0.4921 (3) | 0.9140 (4) | 0.0817 (15) |
| H12  | 0.769460 | 0.542262 | 0.926604 | 0.098*  |
| C21  | 0.6114 (5) | 0.4620 (3) | 0.8266 (4) | 0.0720 (13) |
| H13  | 0.637933 | 0.492736 | 0.782642 | 0.086*  |
| C22  | 0.4359 (4) | 0.1070 (3) | 0.6970 (3) | 0.0542 (9) |
| C23  | 0.0862 (5) | 0.4408 (2) | 0.7478 (3) | 0.0543 (9) |
| C24  | 0.2210 (5) | 0.4838 (3) | 0.7372 (3) | 0.0607 (10) |
| H14  | 0.286908 | 0.451352 | 0.722033 | 0.073*  |
| C25  | 0.2587 (7) | 0.5761 (3) | 0.7493 (4) | 0.0816 (15) |
| H15  | 0.350439 | 0.604667 | 0.742700 | 0.098*  |
| C26  | 0.1643 (9) | 0.6245 (3) | 0.7705 (4) | 0.099 (2) |
| H16  | 0.189677 | 0.686032 | 0.777275 | 0.119*  |
| C27  | 0.0335 (10) | 0.5829 (4) | 0.7817 (5) | 0.115 (2) |
| H17  | -0.031213 | 0.616375 | 0.796792 | 0.137*  |
| C28  | -0.00074 (8) | 0.4916 (4) | 0.7713 (5) | 0.0931 (18) |
| H18  | -0.098155 | 0.464252 | 0.780230 | 0.112*  |
| C29  | -0.1240 (5) | 0.3099 (3) | 0.6248 (3) | 0.0638 (11) |
| C30  | -0.2398 (7) | 0.2426 (5) | 0.5962 (5) | 0.105 (2) |
| H19  | -0.253912 | 0.198479 | 0.632581 | 0.126*  |
| C31  | -0.3409 (10) | 0.2352 (6) | 0.5141 (6) | 0.139 (3) |
| H20  | -0.425729 | 0.190055 | 0.499432 | 0.167*  |
| C32  | -0.3191 (12) | 0.2902 (7) | 0.4576 (5) | 0.151 (4) |
| H21  | -0.387200 | 0.285053 | 0.402952 | 0.181*  |
| C33  | -0.1974 (12) | 0.3538 (9) | 0.4799 (5) | 0.174 (5) |
| H22  | -0.177257 | 0.392207 | 0.439500 | 0.209*  |
| C34  | -0.0982 (8) | 0.3640 (7) | 0.5639 (4) | 0.135 (3) |
| Atom | U^11 | U^12 | U^13 | U^22 | U^23 | U^33 |
|------|------|------|------|------|------|------|
| Ru1  | 0.03849 (16) | 0.04036 (16) | 0.03340 (15) | −0.00234 (10) | 0.01317 (10) | −0.00263 (10) |
| S1   | 0.0506 (6) | 0.0878 (9) | 0.1451 (14) | 0.0143 (6) | 0.0182 (8) | −0.0414 (9) |
| P1   | 0.0419 (5) | 0.0462 (5) | 0.0400 (4) | 0.0036 (3) | 0.0091 (3) | −0.0047 (3) |
| P2   | 0.0728 (7) | 0.0505 (5) | 0.0496 (5) | −0.0018 (5) | 0.0197 (5) | 0.0032 (4) |
| F1   | 0.203 (5) | 0.074 (2) | 0.084 (2) | −0.002 (2) | 0.041 (3) | −0.0228 (17) |
| F2   | 0.124 (3) | 0.0687 (17) | 0.0681 (17) | −0.0153 (16) | 0.0381 (17) | −0.0117 (14) |
| F3   | 0.154 (3) | 0.077 (2) | 0.084 (2) | 0.015 (2) | 0.038 (2) | 0.0341 (17) |
| F4   | 0.070 (2) | 0.112 (3) | 0.161 (4) | −0.0060 (18) | 0.036 (2) | 0.012 (3) |
| F5   | 0.131 (3) | 0.0773 (19) | 0.0681 (18) | 0.0050 (18) | 0.0212 (18) | 0.0231 (15) |
| F6   | 0.085 (2) | 0.138 (3) | 0.128 (3) | 0.028 (2) | 0.052 (2) | 0.033 (3) |
| O1   | 0.0666 (17) | 0.0576 (16) | 0.0482 (15) | −0.0099 (13) | 0.0226 (13) | 0.0040 (12) |
| N1   | 0.072 (2) | 0.0569 (19) | 0.0380 (15) | −0.0108 (15) | 0.0213 (15) | −0.0055 (13) |
| N2   | 0.0405 (14) | 0.0444 (14) | 0.0352 (13) | −0.0002 (11) | 0.0125 (11) | −0.0058 (11) |
| N3   | 0.0465 (15) | 0.0401 (14) | 0.0353 (13) | 0.0000 (11) | 0.0129 (11) | −0.0014 (11) |
| N4   | 0.0427 (15) | 0.0453 (15) | 0.0388 (14) | 0.0008 (11) | 0.0108 (11) | −0.0025 (11) |
| N5   | 0.0460 (17) | 0.0592 (19) | 0.059 (2) | −0.0063 (14) | 0.0095 (14) | 0.0053 (15) |
| N6   | 0.0459 (16) | 0.0557 (17) | 0.0500 (17) | 0.0058 (13) | 0.0163 (13) | −0.0058 (14) |
| C1   | 0.089 (3) | 0.073 (3) | 0.040 (2) | −0.013 (2) | 0.024 (2) | −0.0009 (18) |
| C2   | 0.081 (3) | 0.076 (3) | 0.0365 (19) | 0.002 (2) | 0.0151 (19) | −0.0025 (18) |
| C3   | 0.061 (2) | 0.076 (3) | 0.0411 (19) | −0.001 (2) | 0.0089 (17) | −0.0093 (18) |
| C4   | 0.0473 (19) | 0.060 (2) | 0.0391 (17) | 0.0008 (16) | 0.0126 (15) | −0.0078 (15) |
| C5   | 0.0494 (19) | 0.0501 (18) | 0.0373 (16) | 0.0006 (14) | 0.0166 (14) | −0.0062 (14) |
Geometric parameters (Å, º)

| Bond/Angle | Distance/Angle | Distance/Angle |
|------------|----------------|----------------|
| Ru1—N3     | 1.936 (3)      | C16—C17        | 1.388 (7)      |
| Ru1—N2     | 2.100 (3)      | C16—H10        | 0.9300         |
| Ru1—N4     | 2.105 (3)      | C17—C19        | 1.419 (6)      |
| Ru1—N6     | 2.105 (3)      | C17—C18        | 1.421 (5)      |
| Ru1—O1     | 2.176 (3)      | C19—C20        | 1.338 (8)      |
| Ru1—P1     | 2.3409 (9)     | C19—H11        | 0.9300         |

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S1—C22 1.637 (4) C20—C21 1.421 (7)
P1—C35 1.836 (4) C20—H12 0.9300
P1—C23 1.836 (4) C21—H13 0.9300
P1—C29 1.839 (4) C23—C24 1.377 (6)
P2—F6 1.562 (4) C23—C28 1.380 (7)
P2—F1 1.577 (3) C24—C25 1.393 (6)
P2—F4 1.579 (4) C24—H14 0.9300
P2—F2 1.588 (3) C25—C26 1.346 (9)
P2—F3 1.588 (3) C25—H15 0.9300
P2—F5 1.590 (3) C26—C27 1.340 (10)
N1—C1 1.319 (5) C26—H16 0.9300
N1—C5 1.350 (5) C27—C28 1.381 (8)
N2—C8 1.345 (4) C27—H17 0.9300
N2—C5 1.379 (4) C28—H18 0.9300
N3—C13 1.353 (4) C29—C30 1.328 (7)
N3—C9 1.359 (4) C29—C34 1.355 (9)
N4—C14 1.356 (5) C30—C31 1.392 (9)
N4—C18 1.374 (4) C30—H19 0.9300
N5—C21 1.318 (5) C31—C32 1.298 (13)
N5—C18 1.346 (5) C31—H20 0.9300
N6—C22 1.116 (5) C32—C33 1.324 (15)
C1—C2 1.403 (6) C32—H21 0.9300
C1—H1 0.9300 C33—C34 1.406 (9)
C2—C3 1.355 (6) C33—H22 0.9300
C2—H2 0.9300 C34—H23 0.9300
C3—C4 1.419 (5) C35—C40 1.368 (6)
C3—H3 0.9300 C35—C36 1.376 (6)
C4—C5 1.407 (5) C36—C37 1.370 (7)
C4—C6 1.413 (6) C36—H24 0.9300
C6—C7 1.356 (6) C37—C38 1.346 (8)
C6—H4 0.9300 C37—H25 0.9300
C7—C8 1.404 (5) C38—C39 1.377 (9)
C7—H5 0.9300 C38—H26 0.9300
C8—C9 1.465 (5) C39—C40 1.385 (8)
C9—C10 1.379 (5) C39—H27 0.9300
C10—C11 1.397 (6) C40—H28 0.9300
C10—H6 0.9300 O2—C42 1.19 (2)
C11—C12 1.386 (6) C41—C42 1.47 (3)
C11—H7 0.9300 C41—H29 0.9600
C12—C13 1.374 (5) C41—H30 0.9600
C12—H8 0.9300 C41—H31 0.9600
C13—C14 1.474 (5) C42—C43 1.53 (3)
C14—C15 1.400 (5) C43—H32 0.9600
C15—C16 1.356 (6) C43—H33 0.9600
C15—H9 0.9300 C43—H34 0.9600

N3—Ru1—N2 79.15 (11) C16—C15—H9 120.2
N3—Ru1—N4 79.47 (11) C14—C15—H9 120.2
### Crystallographic Data

| Bond/Angle | Distance/Standard Deviation |
|------------|-----------------------------|
| N2—Ru1—N4  | 158.24 (12)                 |
| N3—Ru1—N6  | 90.12 (13)                  |
| N2—Ru1—N6  | 87.81 (11)                  |
| N4—Ru1—N6  | 88.21 (12)                  |
| N3—Ru1—O1  | 175.58 (11)                 |
| N2—Ru1—O1  | 96.97 (11)                  |
| N4—Ru1—O1  | 104.23 (11)                 |
| N6—Ru1—O1  | 87.59 (13)                  |
| N3—Ru1—P1  | 92.21 (9)                   |
| N2—Ru1—P1  | 91.23 (8)                   |
| N4—Ru1—P1  | 93.61 (8)                   |
| N6—Ru1—P1  | 177.27 (9)                  |
| O1—Ru1—P1  | 89.98 (9)                   |
| C35—P1—C23 | 100.93 (18)                 |
| C35—P1—C29 | 109.5 (2)                   |
| C23—P1—C29 | 101.0 (2)                   |
| C35—P1—Ru1 | 112.05 (13)                 |
| C23—P1—Ru1 | 120.14 (14)                 |
| C29—P1—Ru1 | 112.01 (15)                 |
| F6—P2—F1  | 89.9 (3)                    |
| F6—P2—F4  | 179.6 (3)                   |
| F1—P2—F4  | 90.6 (3)                    |
| F6—P2—F2  | 90.3 (2)                    |
| F1—P2—F2  | 179.7 (3)                   |
| F4—P2—F2  | 89.3 (2)                    |
| F6—P2—F3  | 90.5 (2)                    |
| F1—P2—F3  | 89.7 (2)                    |
| F4—P2—F3  | 89.5 (2)                    |
| F2—P2—F3  | 90.49 (19)                  |
| F6—P2—F5  | 88.4 (2)                    |
| F1—P2—F5  | 89.9 (2)                    |
| F4—P2—F5  | 91.5 (2)                    |
| F2—P2—F5  | 89.90 (18)                  |
| F3—P2—F5  | 178.9 (2)                   |
| C1—N1—C5  | 118.0 (3)                   |
| C8—N2—C5  | 118.0 (3)                   |
| C8—N2—Ru1 | 112.9 (2)                   |
| C5—N2—Ru1 | 129.1 (2)                   |
| C13—N3—C9 | 120.8 (3)                   |
| C13—N3—Ru1| 119.8 (2)                   |
| C9—N3—Ru1 | 119.4 (2)                   |
| C14—N4—C18| 117.6 (3)                   |
| C14—N4—Ru1| 112.3 (2)                   |
| C18—N4—Ru1| 130.1 (2)                   |
| C21—N5—C18| 117.8 (4)                   |
| C22—N6—Ru1| 175.6 (3)                   |
| N1—C1—C2  | 123.9 (4)                   |
| N1—C1—H1  | 118.0                       |

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C2—C1—H1 118.0 C33—C32—H21 120.9
C3—C2—C1 118.7 (4) C32—C33—C34 120.8 (10)
C3—C2—H2 120.6 C32—C33—H22 119.6
C1—C2—H2 120.6 C34—C33—H22 119.6
C2—C3—C4 119.2 (4) C29—C34—C33 121.4 (9)
C2—C3—H3 120.4 C29—C34—H23 119.3
C4—C3—H3 120.4 C33—C34—H23 119.3
C5—C4—C6 118.6 (3) C40—C35—C36 117.2 (4)
C5—C4—C3 117.8 (4) C40—C35—P1 124.4 (3)
C6—C4—C3 123.6 (4) C36—C35—P1 118.0 (3)
N1—C5—N2 116.2 (3) C37—C36—C35 121.4 (9)
N1—C5—C4 122.3 (3) C37—C36—H24 119.1
N2—C5—C4 121.5 (3) C35—C36—H24 119.1
C7—C6—C4 119.4 (3) C38—C37—C36 121.1 (5)
C7—C6—H4 120.3 C38—C37—H25 119.4
C4—C6—H4 120.3 C36—C37—H25 119.4
C6—C7—C8 119.7 (3) C37—C38—C39 118.1 (5)
C6—C7—H5 120.1 C37—C38—H26 120.9
C8—C7—H5 120.1 C39—C38—H26 120.9
N2—C8—C9 115.5 (3) C38—C39—C40 121.0 (5)
N2—C8—C7 122.7 (3) C38—C39—H27 119.5
C7—C8—C9 121.8 (3) C40—C39—H27 119.5
N3—C9—C10 120.6 (3) C35—C40—C39 120.6 (5)
N3—C9—C8 113.0 (3) C35—C40—H28 119.7
C10—C9—C8 126.4 (3) C39—C40—H28 119.7
C9—C10—H6 120.5 C42—C41—H29 109.5
C11—C10—H6 120.5 C42—C41—H30 109.5
C12—C11—C10 119.5 (4) C42—C41—H31 109.5
C12—C11—H7 120.2 H29—C41—H30 109.5
C10—C11—H7 120.2 H29—C41—H31 109.5
C13—C12—C11 119.6 (4) O2—C42—C41 121 (2)
C13—C12—H8 120.2 O2—C42—C43 120 (2)
C11—C12—H8 120.2 C41—C42—C43 118 (2)
C12—C13—C12 120.6 (3) C42—C43—H32 109.5
C3—C13—C12 120.6 (3) C42—C43—H33 109.5
C12—C13—C14 126.6 (3) H32—C43—H33 109.5
N4—C14—C15 122.6 (3) C42—C43—H34 109.5
N4—C14—C13 115.7 (3) H32—C43—H34 109.5
C15—C14—C13 121.7 (3) H33—C43—H34 109.5
C5—N1—C1—C2 0.9 (8) C21—N5—C18—C17 18 (6)
N1—C1—C2—C3 0.7 (8) C14—N4—C18—N5 175.8 (3)
C1—C2—C3—C4 0.3 (7) Ru1—N4—C18—N5 2.1 (5)
C2—C3—C4—C5 2.0 (7) C14—N4—C18—C17 4.3 (5)
C2—C3—C4—C6 −177.3 (4) Ru1—N4—C18—C17 177.8 (3)
C1—N1—C5—N2 −179.2 (4) C16—C17—C18—N5 178.7 (4)
| Bond                  | Angle (°) | Bond                  | Angle (°) |
|-----------------------|-----------|-----------------------|-----------|
| C1—N1—C5—C4          | 1.9 (6)   | C19—C17—C18—N5       | 2.1 (6)   |
| C8—N2—C5—N1         | −175.2 (3)| C16—C17—C18—N4       | 1.5 (6)   |
| Ru1—N2—C5—N1        | 5.5 (5)   | C19—C17—C18—N4       | −177.8 (4)|
| C8—N2—C5—C4         | 3.6 (5)   | C16—C17—C19—C20      | −179.6 (5)|
| Ru1—N2—C5—C4        | −175.6 (3)| C18—C17—C19—C20      | −0.4 (8)  |
| C6—C4—C5—N1         | 176.5 (4) | C17—C19—C20—C21      | −1.4 (9)  |
| C3—C4—C5—N1         | −2.9 (6)  | C18—N5—C21—C20       | −0.2 (8)  |
| C6—C4—C5—N2         | −2.3 (6)  | C19—C20—C21—N5       | 1.8 (9)   |
| C3—C4—C5—N2         | 178.3 (4) | C35—P1—C23—C24       | 140.2 (4) |
| C5—C4—C6—C7         | −0.2 (6)  | C29—P1—C23—C24       | −107.1 (4)|
| C3—C4—C6—C7         | 179.2 (4) | Ru1—P1—C23—C24       | 16.6 (4)  |
| C4—C6—C7—C8         | 1.2 (6)   | C35—P1—C23—C28       | −42.5 (5) |
| C5—N2—C8—C7         | −2.6 (5)  | C29—P1—C23—C28       | 70.1 (5)  |
| Ru1—N2—C8—C7        | 176.8 (3) | Ru1—P1—C23—C28       | −166.2 (4)|
| C5—N2—C8—C9         | 178.4 (3) | C28—C23—C24—C25      | −0.7 (7)  |
| Ru1—N2—C8—C9        | −2.2 (4)  | P1—C23—C24—C25       | 176.6 (4) |
| C6—C7—C8—N2         | 0.2 (6)   | C23—C24—C25—C26      | −0.7 (7)  |
| C6—C7—C8—C9         | 179.2 (4) | C24—C25—C26—C27      | 1.3 (9)   |
| C13—N3—C9—C10       | 1.8 (6)   | C25—C26—C27—C28      | −0.5 (12) |
| Ru1—N3—C9—C10       | 179.3 (3) | C24—C23—C28—C27      | 1.4 (9)   |
| C13—N3—C9—C8        | −176.9 (3)| P1—C23—C28—C27       | −175.9 (6)|
| Ru1—N3—C9—C8        | 0.5 (4)   | C26—C27—C28—C23      | −0.9 (12) |
| N2—C8—C9—N3         | 1.2 (5)   | C35—P1—C23—C30       | −48.5 (6) |
| C7—C8—C9—N3         | −177.8 (3)| C23—P1—C29—C30       | −154.4 (6)|
| N2—C8—C9—C10        | −177.4 (4)| Ru1—P1—C29—C30       | 76.5 (6)  |
| C7—C8—C9—C10        | 3.6 (6)   | C35—P1—C29—C34       | 147.9 (5) |
| N3—C9—C10—C11       | −0.9 (7)  | C23—P1—C29—C34       | 42.0 (6)  |
| C8—C9—C10—C11       | 177.7 (5) | Ru1—P1—C29—C34       | −87.1 (6) |
| C9—C10—C11—C12      | −0.3 (9)  | C34—C29—C30—C31      | −9.3 (11) |
| C10—C11—C12—C13     | 0.5 (9)   | P1—C29—C30—C31       | −173.3 (7)|
| C9—N3—C13—C12       | −1.6 (6)  | C29—C30—C31—C32      | 6.4 (15)  |
| Ru1—N3—C13—C12      | −179.0 (4)| C30—C31—C32—C33      | 0.2 (17)  |
| C9—N3—C13—C14       | 177.5 (3) | C31—C32—C33—C34      | −2.9 (18) |
| Ru1—N3—C13—C14      | 0.1 (5)   | C30—C29—C34—C33      | 6.4 (12)  |
| C11—C12—C13—N3      | 0.4 (8)   | P1—C29—C34—C33       | 171.9 (8) |
| C11—C12—C13—C14     | −178.6 (5)| C32—C33—C34—C29      | −0.5 (17) |
| C18—N4—C14—C15      | 4.0 (6)   | C23—P1—C35—C40       | 134.2 (5) |
| Ru1—N4—C14—C15      | −177.8 (4)| C29—P1—C35—C40       | 28.2 (6)  |
| C18—N4—C14—C13      | −177.5 (3)| Ru1—P1—C35—C40       | −96.7 (5) |
| Ru1—N4—C14—C13      | 0.7 (4)   | C23—P1—C35—C36       | −51.9 (4) |
| N3—C13—C14—N4       | −0.6 (5)  | C29—P1—C35—C36       | −157.9 (4)|
| C12—C13—C14—N4      | 178.5 (5) | Ru1—P1—C35—C36       | 77.2 (4)  |
| N3—C13—C14—C15      | 177.9 (4) | C40—C35—C36—C37      | 1.1 (9)   |
| C12—C13—C14—C15     | −3.0 (8)  | P1—C35—C36—C37       | −173.2 (5)|
| N4—C14—C15—C16      | −0.6 (8)  | C35—C36—C37—C38      | −0.1 (10) |
| C13—C14—C15—C16     | −179.1 (5)| C36—C37—C38—C39      | −1.3 (11) |
| C14—C15—C16—C17     | −2.4 (8)  | C37—C38—C39—C40      | 1.8 (13)  |
| C15—C16—C17—C19     | −178.9 (5)| C36—C35—C40—C39      | −0.6 (11) |
C15—C16—C17—C18  2.0 (8)  P1—C35—C40—C39  173.4 (7)
C21—N5—C18—N4  178.1 (4)  C38—C39—C40—C35 −0.9 (14)

Hydrogen-bond geometry (Å, °)

| D—H···A         | D—H | H···A | D···A | D—H···A |
|-----------------|------|-------|-------|---------|
| C10—H6···F5i    | 0.93 | 2.45  | 3.369 (6) | 170     |
| C15—H9···F2     | 0.93 | 2.45  | 3.345 (6) | 162     |
| C21—H13···O2    | 0.93 | 2.59  | 3.213 (14) | 124     |
| C24—H14···O1    | 0.93 | 2.43  | 3.210 (5) | 141     |
| C24—H14···N5    | 0.93 | 2.43  | 3.144 (6) | 134     |
| C25—H15···F4ii  | 0.93 | 2.54  | 3.347 (7) | 145     |
| C41—H30···F1ii  | 0.96 | 2.40  | 3.26 (3)  | 150     |

Symmetry codes: (i) −x, −y, −z+2; (ii) −x+1, −y+1, −z+2.

trans-[2,6-Bis(1,8-naphthyridin-2-yl)pyridine-κN,N',N'']bis(pyridine-κN)(thiocyanato-κN)ruthenium(II) thiocyanate (II)

Crystal data

[Ru(NCS)(C21H13N5)(C5H5N)2]NCS  
F(000) = 1440.00  
M_r = 710.79  
Monoclinic, P2_1/c  
a = 12.6556 (10) Å  
b = 14.0986 (7) Å  
c = 17.4421 (14) Å  
β = 108.535 (3)°  
V = 2950.7 (4) Å³  
Z = 4  
Mo Kα radiation, λ = 0.71075 Å  
Cell parameters from 7649 reflections  
θ = 3.1–27.6°  
µ = 0.72 mm⁻¹  
T = 93 K  
Platelet, purple  
0.25 × 0.15 × 0.05 mm

Data collection

Rigaku Saturn724  
diffractometer  
Detector resolution: 28.626 pixels mm⁻¹  
6758 independent reflections  
6058 reflections with F² > 2σ(F²)  
θ_max = 27.5°, θ_min = 3.1°  
h = −16→16  
k = −18→18  
l = −22→21  
30135 measured reflections

Refinement

Refinement on F²  
R[F² > 2σ(F²)] = 0.036  
wR(F²) = 0.091  
S = 1.10  
6758 reflections  
406 parameters  
0 restraints  
H-atom parameters constrained  
Secondary atom site location: difference Fourier map  
Hydrogen site location: inferred from neighbouring sites  
w = 1/[σ(F_c)^2 + (0.0451P)^2 + 2.9803P] 
where P = (F_c^2 + 2F_s^2)/3  
(Δ/σ)_max = 0.001  
Δρ_max = 1.13 e Å⁻³  
Δρ_min = −0.81 e Å⁻³  

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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.

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of F^2 > 2.0 sigma(F^2) is used only for calculating R-factor (gt).

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

|    | x     | y     | z     | Uiso/UAeq |
|----|-------|-------|-------|-----------|
| Ru1| 0.73332 (2) | 0.38197 (2) | 0.79490 (2) | 0.01220 (7) |
| S1 | 0.39862 (5)  | 0.39265 (5)  | 0.87218 (4)  | 0.02286 (14) |
| S2 | 1.08750 (7)  | 0.12965 (7)  | 0.89031 (6)  | 0.0466 (2)   |
| N1 | 0.70294 (18) | 0.38857 (15) | 0.98054 (13) | 0.0213 (4)   |
| N2 | 0.83872 (16) | 0.38102 (13) | 0.91797 (12) | 0.0155 (4)   |
| N3 | 0.88229 (16) | 0.37934 (13) | 0.78244 (13) | 0.0161 (4)   |
| N4 | 0.69378 (17) | 0.37739 (13) | 0.66605 (12) | 0.0155 (4)   |
| N5 | 0.50056 (17) | 0.38259 (15) | 0.62868 (13) | 0.0195 (4)   |
| N6 | 0.70364 (15) | 0.52961 (14) | 0.79703 (11) | 0.0144 (4)   |
| N7 | 0.71689 (16) | 0.23463 (14) | 0.79725 (11) | 0.0148 (4)   |
| N8 | 0.57779 (16) | 0.38875 (13) | 0.81029 (12) | 0.0150 (4)   |
| N9 | 1.1118 (3)   | 0.1261 (2)   | 1.0511 (3)   | 0.0605 (10)  |
| C1 | 0.6735 (2)   | 0.38898 (19) | 1.04670 (16) | 0.0250 (6)   |
| H1 | 0.596645     | 0.395157     | 1.040937     | 0.030*       |
| C2 | 0.7502 (2)   | 0.38073 (18) | 1.12584 (16) | 0.0257 (6)   |
| H2 | 0.725046     | 0.381745     | 1.171672     | 0.031*       |
| C3 | 0.8603 (2)   | 0.37134 (19) | 1.13490 (16) | 0.0263 (6)   |
| H3 | 0.913218     | 0.365204     | 1.187311     | 0.032*       |
| C4 | 0.8955 (2)   | 0.37077 (18) | 1.06568 (16) | 0.0222 (5)   |
| C5 | 0.8121 (2)   | 0.37965 (16) | 0.98896 (15) | 0.0170 (5)   |
| C6 | 1.0075 (2)   | 0.3633 (2)   | 1.06873 (17) | 0.0302 (6)   |
| H4 | 1.064516     | 0.355198     | 1.119123     | 0.036*       |
| C7 | 1.0338 (2)   | 0.3677 (2)   | 0.99887 (17) | 0.0287 (6)   |
| H5 | 1.109374     | 0.363661     | 1.000289     | 0.034*       |
| C8 | 0.9484 (2)   | 0.37788 (17) | 0.92474 (16) | 0.0192 (5)   |
| C9 | 0.9741 (2)   | 0.38180 (16) | 0.84863 (16) | 0.0189 (5)   |
| C10| 1.0804 (2)   | 0.38683 (18) | 0.84086 (17) | 0.0236 (5)   |
| H6 | 1.144589     | 0.388480     | 0.887533     | 0.028*       |
| C11| 1.0912 (2)   | 0.38939 (18) | 0.76456 (18) | 0.0257 (6)   |
| H7 | 1.162986     | 0.394404     | 0.758536     | 0.031*       |
| C12| 0.9974 (2)   | 0.38464 (18) | 0.69684 (17) | 0.0236 (5)   |
| H8 | 1.004151     | 0.385025     | 0.644116     | 0.028*       |
| C13| 0.8932 (2)   | 0.37929 (16) | 0.70748 (15) | 0.0181 (5)   |
| C14| 0.7866 (2)   | 0.37476 (16) | 0.64229 (16) | 0.0192 (5)   |
| C15| 0.7840 (2)   | 0.3661 (2)   | 0.56132 (16) | 0.0258 (6)   |
| H9 | 0.851351     | 0.365671     | 0.548224     | 0.031*       |
### Atomic displacement parameters (Å²)

|   | U¹¹ | U¹² | U¹³ | U²² | U²³ | U³³ |
|---|-----|-----|-----|-----|-----|-----|
|Ru1| 0.01117 (10) | 0.01297 (10) | 0.01255 (10) | 0.00016 (6) | 0.00390 (7) | 0.00024 (7) |
|S1 | 0.0170 (3) | 0.0297 (3) | 0.0251 (3) | −0.0005 (2) | 0.0111 (2) | −0.0020 (3) |
|S2 | 0.0280 (4) | 0.0616 (6) | 0.0502 (5) | 0.0079 (4) | 0.0122 (4) | 0.0023 (4) |
|N1 | 0.0198 (10) | 0.0278 (11) | 0.0160 (10) | 0.0031 (8) | 0.0055 (8) | 0.0019 (8) |
|N2 | 0.0145 (9) | 0.0156 (9) | 0.0144 (10) | −0.0001 (7) | 0.0020 (8) | 0.0011 (7) |
|N3 | 0.0155 (9) | 0.0147 (9) | 0.0196 (10) | −0.0002 (7) | 0.0076 (8) | 0.0009 (8) |
|N4 | 0.0182 (9) | 0.0157 (9) | 0.0139 (9) | 0.0003 (7) | 0.0069 (8) | 0.0010 (7) |
|N5 | 0.0183 (10) | 0.0246 (11) | 0.0153 (10) | 0.0000 (8) | 0.0049 (8) | −0.0010 (8) |
|N6 | 0.0131 (9) | 0.0137 (9) | 0.0141 (9) | 0.0001 (7) | 0.0012 (7) | 0.0013 (7) |
|N7 | 0.0168 (9) | 0.0139 (9) | 0.0149 (9) | −0.0010 (7) | 0.0069 (8) | −0.0012 (7) |
|N8 | 0.0143 (9) | 0.0163 (9) | 0.0138 (9) | 0.0001 (7) | 0.0036 (7) | −0.0001 (7) |
|N9 | 0.0074 (2) | 0.0450 (19) | 0.092 (3) | −0.0064 (16) | 0.068 (2) | −0.0125 (19) |
### Geometric parameters (Å, °)

| Bond/Distance | Value   | Bond/Distance | Value   | Bond/Distance | Value   | Bond/Distance | Value   |
|---------------|---------|---------------|---------|---------------|---------|---------------|---------|
| Ru1—N3        | 1.966 (2)| C10—C11       | 1.381 (4)| Ru1—N8        | 1.966 (2)| C10—H6        | 0.9500  |
| Ru1—N8        | 2.069 (2)| C10—N6        | 2.0824 (19)| Ru1—N7       | 2.0893 (19)| C11—C12       | 1.384 (4)|
| Ru1—N6        | 2.0824 (19)| Ru1—N7       | 2.0893 (19)| Ru1—N7       | 2.0893 (19)| C11—H7        | 0.9500  |
| Ru1—N2        | 2.137 (2)| C12—C13       | 1.391 (3)| Ru1—N4        | 2.142 (2)| C12—H8        | 0.9500  |
| S1—C32        | 1.647 (2)| C13—C14       | 1.464 (4)| S2—C33        | 1.715 (4)| C14—C15       | 1.407 (4)|
| N1—C1         | 1.320 (3)| C15—C16       | 1.353 (4)| N1—C5         | 1.348 (3)| C15—H9        | 0.9500  |
| N2—C8         | 1.355 (3)| C16—C17       | 1.410 (4)| N2—C5         | 1.383 (3)| C16—H10       | 0.9500  |
| Bond          | Distance (Å) | Bond          | Distance (Å) | Bond          | Distance (Å) |
|--------------|-------------|--------------|-------------|--------------|-------------|
| N3—C9        | 1.353 (3)   | C17—C19      | 1.410 (4)   |               |              |
| N3—C13       | 1.358 (3)   | C17—C18      | 1.423 (3)   |               |              |
| N4—C14       | 1.365 (3)   | C19—C20      | 1.357 (4)   |               |              |
| N4—C18       | 1.382 (3)   | C19—H11      | 0.9500      |               |              |
| N5—C21       | 1.323 (3)   | C20—C21      | 1.412 (4)   |               |              |
| N5—C18       | 1.351 (3)   | C20—H12      | 0.9500      |               |              |
| N6—C26       | 1.350 (3)   | C21—H13      | 0.9500      |               |              |
| N6—C22       | 1.352 (3)   | C22—C23      | 1.377 (4)   |               |              |
| N7—C27       | 1.348 (3)   | C22—H14      | 0.9500      |               |              |
| N7—C31       | 1.361 (3)   | C23—C24      | 1.384 (4)   |               |              |
| N8—C32       | 1.160 (3)   | C23—H15      | 0.9500      |               |              |
| N9—C33       | 1.009 (5)   | C24—C25      | 1.387 (4)   |               |              |
| C1—C2        | 1.417 (4)   | C24—H16      | 0.9500      |               |              |
| C1—H1        | 0.9500      | C25—C26      | 1.387 (4)   |               |              |
| C2—C3        | 1.358 (4)   | C25—H17      | 0.9500      |               |              |
| C2—H2        | 0.9500      | C26—H18      | 0.9500      |               |              |
| C3—C4        | 1.413 (4)   | C27—C28      | 1.390 (3)   |               |              |
| C3—H3        | 0.9500      | C27—H19      | 0.9500      |               |              |
| C4—C6        | 1.407 (4)   | C28—C29      | 1.379 (4)   |               |              |
| C4—C5        | 1.422 (3)   | C28—H20      | 0.9500      |               |              |
| C6—C7        | 1.363 (4)   | C29—C30      | 1.389 (4)   |               |              |
| C6—H4        | 0.9500      | C29—H21      | 0.9500      |               |              |
| C7—C8        | 1.405 (4)   | C30—C31      | 1.381 (3)   |               |              |
| C7—H5        | 0.9500      | C30—H22      | 0.9500      |               |              |
| C8—C9        | 1.465 (4)   | C31—H23      | 0.9500      |               |              |
| C9—C10       | 1.396 (3)   |               |              |               |              |
| N3—Ru1—N8    | 178.11 (8)  | C10—C11—H7   | 120.0       |               |              |
| N3—Ru1—N6    | 92.43 (7)   | C12—C11—H7   | 120.0       |               |              |
| N8—Ru1—N6    | 85.99 (7)   | C11—C12—C13  | 118.7 (2)   |               |              |
| N3—Ru1—N7    | 95.07 (7)   | C11—C12—H8   | 120.6       |               |              |
| N8—Ru1—N7    | 86.49 (7)   | C13—C12—H8   | 120.6       |               |              |
| N6—Ru1—N7    | 172.39 (7)  | N3—C13—C12   | 121.3 (2)   |               |              |
| N3—Ru1—N2    | 78.26 (8)   | N3—C13—C14   | 113.4 (2)   |               |              |
| N8—Ru1—N2    | 100.68 (8)  | C12—C13—C14  | 125.3 (2)   |               |              |
| N6—Ru1—N2    | 89.82 (7)   | N4—C14—C15   | 124.0 (2)   |               |              |
| N7—Ru1—N2    | 90.47 (7)   | N4—C14—C13   | 115.6 (2)   |               |              |
| N3—Ru1—N4    | 78.22 (8)   | C15—C14—C13  | 120.3 (2)   |               |              |
| N8—Ru1—N4    | 102.88 (8)  | C16—C15—C14  | 119.3 (2)   |               |              |
| N6—Ru1—N4    | 92.82 (7)   | C16—C15—H9   | 120.3       |               |              |
| N7—Ru1—N4    | 89.95 (7)   | C14—C15—H9   | 120.3       |               |              |
| N2—Ru1—N4    | 156.42 (8)  | C15—C16—C17  | 119.3 (2)   |               |              |
| C1—N1—C5     | 118.0 (2)   | C15—C16—H10  | 120.4       |               |              |
| C8—N2—C5     | 117.1 (2)   | C17—C16—H10  | 120.4       |               |              |
| C8—N2—Ru1    | 112.50 (16) | C16—C17—C19  | 122.5 (2)   |               |              |
| C5—N2—Ru1    | 130.37 (16) | C16—C17—C18  | 119.4 (2)   |               |              |
| C9—N3—C13    | 119.9 (2)   | C19—C17—C18  | 118.1 (2)   |               |              |
| C9—N3—Ru1    | 119.92 (17) | N5—C18—N4    | 116.4 (2)   |               |              |
C13—N3—Ru1 120.09 (16) N5—C18—C17 122.3 (2)  
C14—N4—C18 116.5 (2) N4—C18—C17 121.3 (2)  
C14—N4—Ru1 112.51 (16) C20—C19—C17 119.5 (2)  
C18—N4—Ru1 130.93 (16) C20—C19—H11 120.2  
C21—N5—C18 117.1 (2) C17—C19—H11 120.2  
C26—N6—C22 117.6 (2) C19—C20—C21 118.0 (3)  
C26—N6—Ru1 123.63 (16) C19—C20—H12 121.0  
C22—N6—Ru1 118.65 (16) C21—C20—H12 121.0  
C27—N7—C31 117.6 (2) N5—C21—C20 125.0 (2)  
C27—N7—Ru1 122.59 (16) N5—C21—H13 117.5  
C31—N7—Ru1 119.71 (16) C20—C21—H13 117.5  
C32—N8—Ru1 166.03 (19) N6—C22—C23 122.8 (2)  
N1—C1—C2 123.7 (3) N6—C22—H14 118.6  
N1—C1—H1 118.1 C23—C22—H14 118.6  
C2—C1—H1 118.1 C22—C23—C24 119.3 (2)  
C3—C2—C1 118.7 (3) C22—C23—H15 120.3  
C3—C2—H2 120.6 C24—C23—H15 120.3  
C1—C2—H2 120.6 C23—C24—C25 118.7 (2)  
C2—C3—C4 119.4 (2) C23—C24—H16 120.6  
C2—C3—H3 120.3 C25—C24—H16 120.6  
C4—C3—H3 120.3 C26—C25—C24 118.9 (2)  
C6—C4—C3 123.8 (2) C26—C25—H17 120.5  
C6—C4—C5 118.7 (2) C24—C25—H17 120.5  
C3—C4—C5 117.6 (2) N6—C26—C25 122.6 (2)  
N1—C5—N2 115.7 (2) N6—C26—H18 118.7  
N1—C5—C4 122.6 (2) C25—C26—H18 118.7  
N2—C5—C4 121.7 (2) N7—C27—C28 122.8 (2)  
C7—C6—C4 119.5 (2) N7—C27—H19 118.6  
C7—C6—H4 120.2 C28—C27—H19 118.6  
C4—C6—H4 120.2 C28—C27—C29 119.1 (2)  
C6—C7—C8 119.5 (2) C29—C28—C27 120.4  
C6—C7—H5 120.3 C29—C28—H20 120.4  
C8—C7—H5 120.3 C27—C28—H20 120.4  
N2—C8—C7 123.4 (2) C28—C29—C30 118.7 (2)  
N2—C8—C9 115.9 (2) C28—C29—H21 120.7  
C7—C8—C9 120.7 (2) C30—C29—H21 120.7  
N3—C9—C10 120.7 (2) C31—C30—C29 119.5 (2)  
N3—C9—C8 113.2 (2) C31—C30—H22 120.2  
C10—C9—C8 126.1 (2) C29—C30—H22 120.2  
C11—C10—C9 119.2 (2) N7—C31—C30 122.3 (2)  
C11—C10—H6 120.4 C30—C31—H23 118.9  
C9—C10—H6 120.4 N8—C32—S1 179.0 (2)  
C10—C11—C12 120.1 (2) N9—C33—S2 178.4 (4)  
C5—N1—C1—C2 0.1 (4) Ru1—N4—C14—C15 176.3 (2)  
N1—C1—C2—C3 −0.4 (4) C18—N4—C14—C13 179.1 (2)  
C1—C2—C3—C4 0.5 (4) Ru1—N4—C14—C13 −2.3 (2)  
C2—C3—C4—C6 178.7 (3) N3—C13—C14—N4 4.0 (3)
C2—C3—C4—C5  
-0.4 (4)  
C1—N1—C5—N2  
-179.1 (2)  
C1—N1—C5—C4  
0.0 (4)  
C8—N2—C5—N1  
176.2 (2)  
Ru1—N2—C5—N1  
-6.5 (3)  
Ru1—N2—C5—C4  
-2.9 (3)  
Ru1—N2—C5—C4  
174.35 (17)  
C6—C4—C5—N1  
-179.0 (2)  
C6—C4—C5—N2  
0.0 (4)  
C6—C4—C5—N2  
179.2 (2)  
C3—C4—C5—N1  
0.1 (4)  
C3—C4—C5—N2  
0.0 (4)  
C3—C4—C5—N1  
179.2 (2)  
C3—C4—C6—C7  
-177.0 (3)  
C5—C4—C6—C7  
2.1 (4)  
C4—C6—C7—C8  
-1.2 (4)  
C5—N2—C8—C7  
3.9 (3)  
Ru1—N2—C8—C7  
-173.8 (2)  
C5—N2—C8—C7  
-178.5 (2)  
Ru1—N2—C8—C7  
3.7 (2)  
C6—C7—C8—N2  
-1.9 (4)  
C6—C7—C8—N2  
179.3 (3)  
C13—N3—C9—C8  
1.7 (3)  
Ru1—N3—C9—C8  
-179.3 (3)  
C13—N3—C9—C8  
1.7 (3)  
Ru1—N3—C9—C8  
5.1 (3)  
N2—C8—C9—N3  
-5.7 (3)  
N2—C8—C9—N3  
171.9 (2)  
C7—C8—C9—N3  
174.8 (2)  
N2—C8—C9—N3  
-7.5 (4)  
C7—C8—C9—N3  
0.1 (4)  
C8—C9—C10—C11  
179.5 (2)  
C9—C10—C11—C12  
-1.6 (4)  
C10—C11—C12—C13  
1.3 (4)  
C9—N3—C13—C12  
-2.0 (3)  
Ru1—N3—C13—C12  
175.11 (18)  
C9—N3—C13—C12  
179.0 (2)  
Ru1—N3—C13—C12  
-3.9 (3)  
C11—C12—C13—N3  
0.5 (4)  
C11—C12—C13—C14  
179.4 (2)  
C18—N4—C14—C15  
-2.3 (3)

Hydrogen-bond geometry (Å, °)

| D—H···A | D—H | H···A | D···A | D—H···A |
|---------|-----|------|-------|---------|
| C12—H8···N9i | 0.95 | 2.43 | 3.305 (5) | 152 |
| C20—H12···S2ii | 0.95 | 2.73 | 3.629 (3) | 159 |
| Bond          | r (Å) | d (Å) | d(H···X) (Å) | D angles (°) |
|--------------|-------|-------|-------------|-------------|
| C22—H14···N1 | 0.95  | 2.51  | 3.391 (3)   | 154         |
| C27—H19···S2 | 0.95  | 2.76  | 3.479 (3)   | 133         |

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