

# Studies of $\kappa^2$ - and $\kappa^3$ -tripyridylamine complexes of ruthenium and $\pi$ -stacking by pyridyls

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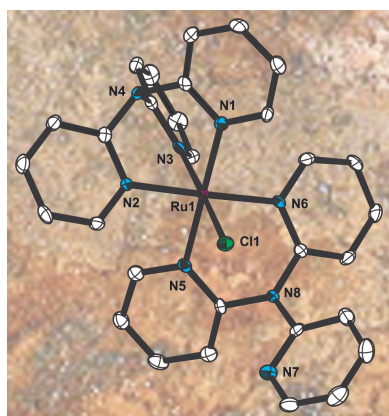
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The reaction of tris(pyridin-2-yl)amine with  $[\text{CyRuCl}_2]_2$  (Cy = *p*-isopropyltoluene or cymene) in refluxing diglyme led to the formation of *cis*- $[\text{RuCl}_2\{\kappa^2\text{-(2-py)}_3\text{N}\}_2]\cdot\text{CHCl}_3$  (**1a**) after recrystallization from chloroform/pentane, or *cis*-dichloridobis[tris(pyridin-2-yl)amine- $\kappa^2N,N'$ ]ruthenium(II) dichloromethane disolvate,  $[\text{RuCl}_2(\text{C}_{15}\text{H}_{12}\text{N}_4)_2]\cdot 2\text{CH}_2\text{Cl}_2$  or *cis*- $[\text{RuCl}_2\{\kappa^2\text{-(2-py)}_3\text{N}\}_2]\cdot 2\text{CH}_2\text{Cl}_2$  (**1b**). Treatment of **1a** with one equivalent of silver(I) hexafluoroantimonate in dichloromethane gave  $[\text{RuCl}\{\kappa^2\text{-(2-py)}_3\text{N}\}\{\kappa^3\text{-(2-py)}_3\text{N}\}][\text{SbF}_6]\cdot\text{CH}_2\text{Cl}_2$  (**2a**). Crystallization of **2a** from chloroform provided chlorido[tris(pyridin-2-yl)amine- $\kappa^2N,N'$ ][tris(pyridin-2-yl)amine- $\kappa^3N,N',N''$ ]ruthenium(II) hexafluoroantimonate chloroform monosolvate,  $[\text{RuCl}(\text{C}_{15}\text{H}_{12}\text{N}_4)_2][\text{SbF}_6]\cdot\text{CHCl}_3$  or  $[\text{RuCl}\{\kappa^2\text{-(2-py)}_3\text{N}\}\{\kappa^3\text{-(2-py)}_3\text{N}\}][\text{SbF}_6]\cdot\text{CHCl}_3$  (**2b**). Complex **2a** reacted with a further equivalent of silver(I) hexafluoroantimonate to give  $[\text{Ru}\{\kappa^3\text{-(2-py)}_3\text{N}\}_2][\text{SbF}_6]_2$  (**3**). The reaction of  $(2\text{-py})_3\text{N}$  with  $[\text{CyRuCl}_2]_2$  in dichloromethane followed by treatment with excess sodium hexafluoroantimonate gave the known complex  $[\text{CyRuCl}\{\kappa^2\text{-(2-py)}_3\text{N}\}][\text{SbF}_6]$  (**4**). Complex **2** is a rare example of a complex containing both  $\kappa^2$ - and  $\kappa^3$ -(2-py)<sub>3</sub>N. Intramolecular  $\pi$ -stacking interactions determine the orientation of the free pyridyl in the  $\kappa^2$  complexes. An interesting encapsulation of methylene chloride hydrogen-bonded tetramers was noted in one case.

## 1. Introduction

Considerable attention has been directed toward the polypyridyl complexes of ruthenium, especially with respect to their unusual photochemical and electrochemical properties (Rutherford *et al.*, 1994; Reitsma & Keene, 1993; Bessel *et al.*, 1993; Sahni *et al.*, 1993; Strouse *et al.*, 1992; Bigozzi *et al.*, 1992; Kalyanasundaram, 1982; Anderson *et al.*, 1994; Collin *et al.*, 1989; Juris *et al.*, 1988; Balzani *et al.*, 2006; Colasson *et al.*, 2016). Included in these studies are complexes containing the *fac*-tridentate ligands tris(pyridin-2-yl)*X* [*X* = N (amine), P (phosphane), CH (methane) or COH (methanol)], which have the ability to bind metals in either a  $\kappa^2$  or a  $\kappa^3$  fashion (Keene *et al.*, 1988*a,b,c*, 1991; Moritz *et al.*, 1988). In contrast to tris(pyridin-2-yl)methane that has produced predominantly  $\kappa^3$  complexes, the presence of the central N atom in tris(pyridin-2-yl)amine, or  $(2\text{-py})_3\text{N}$ , leads to a propensity to produce  $\kappa^2$  complexes (Mosny *et al.*, 1995; Tang *et al.*, 2015), even though there are reports that it can form tridentate complexes (Szelke *et al.*, 2009; Keene *et al.*, 1988*a*). Although one might anticipate a relatively strong donor character from the binding of nitrogen, such ligands are also known to stabilize metals in low oxidation states, including cobalt(I) (Reitsma & Keene, 1994; Hafeli & Keene, 1988). Recently, ligands of this type have been used in the preparation of spin-crossover  $\text{Fe}^{\text{II}}$  materials (Cuza *et al.*, 2021). Nevertheless, prior to this work, there



**Table 1**

Experimental details.

Experiments were carried out at 93 K with Mo  $K\alpha$  radiation. Absorption was corrected for by multi-scan methods (*CrysAlis PRO*; Rigaku OD, 2019). H-atom parameters were constrained.

	<b>1b</b>	<b>2b</b>
Crystal data		
Chemical formula	[RuCl <sub>2</sub> (C <sub>15</sub> H <sub>12</sub> N <sub>4</sub> ) <sub>2</sub> ] $\cdot$ 2CH <sub>2</sub> Cl <sub>2</sub>	[RuCl(C <sub>15</sub> H <sub>12</sub> N <sub>4</sub> ) <sub>2</sub> ][SbF <sub>6</sub> ] $\cdot$ CHCl <sub>3</sub>
$M_r$	838.39	988.21
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/n$
$a, b, c$ (Å)	11.2435 (7), 11.4038 (7), 13.6340 (7)	8.3209 (3), 27.3213 (10), 15.7839 (6)
$\alpha, \beta, \gamma$ (°)	74.278 (5), 75.995 (5), 84.642 (5)	90, 99.554 (4), 90
$V$ (Å <sup>3</sup> )	1631.99 (17)	3538.5 (2)
$Z$	2	4
$\mu$ (mm <sup>-1</sup> )	1.01	1.56
Crystal size (mm)	0.37 $\times$ 0.29 $\times$ 0.2	0.2 $\times$ 0.04 $\times$ 0.01
Data collection		
Diffractometer	Rigaku Mercury275R CCD	Dectris Pilatus 3R
$T_{\min}, T_{\max}$	0.926, 1.000	0.783, 1.000
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	34353, 9877, 6726	32718, 8658, 6339
$R_{\text{int}}$	0.093	0.067
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.714	0.667
Refinement		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.061, 0.108, 1.03	0.048, 0.081, 1.08
No. of reflections	9877	8658
No. of parameters	424	460
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.97, -0.76	0.98, -1.31

Computer programs: *CrysAlis PRO* (Rigaku OD, 2019), *SHELXT2014* (Sheldrick, 2015a), *olex2.solve* (Bourhis *et al.*, 2015), *SHELXL2018* (Sheldrick, 2015b), and *OLEX2* (Dolomanov *et al.*, 2009).

hasn't been an example of a complex containing both a  $\kappa^2$  and a  $\kappa^3$  ligand in the same complex.

In the  $\kappa^3$ -binding mode, these ligands are six-electron-donor analogues of ligands such as  $\eta^6$ -benzene derivatives, tripyrazolylborate, and  $\eta^5$ -cyclopentadienide. Our interest in the complexes of these ligands is based upon their electron-donating abilities as *fac*- $\kappa^3$  ligands which stabilize complexes with positive charges, such as [W{tris(pyridin-2-yl)methane}-(CO)(NO)<sub>2</sub>]<sup>2+</sup> (Faller & Ma, 1991). This complex has proven to be an effective Lewis acid catalyst in the addition of silyl enol ethers to ketones (Faller & Gundersen, 1993), as there is facile loss of the CO ligand from the 18-electron tungsten complex. The complex [CpRu(P)<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>)]<sup>+</sup>, where (P)<sub>2</sub> is (PPh<sub>3</sub>)<sub>2</sub> or chiraphos [(2*S*,3*S*)-2,3-bis(diphenylphophanyl)butane], was also found to be an effective Lewis acid catalyst, in this case for a hetero Diels–Alder reaction, where the active species is formed by the loss of ethylene to give a 16-electron complex (Faller & Smart, 1989). We wished to extend the (pyridin-2-yl)<sub>3</sub>X chemistry to ruthenium, with the express purpose of preparing complexes which might act as Lewis acid catalysts. (2-py)<sub>3</sub>N was chosen over the other *fac*-tridentate ligands owing to its ease of preparation using a high-yield variation of a published one-step synthesis from commercially available starting materials (Mosny *et al.*, 1995). We have developed an improved synthesis of ruthenium complexes of (2-py)<sub>3</sub>N based on [CyRuCl<sub>2</sub>]<sub>2</sub>. The relative ease of forming these  $\kappa^2$ -(2-py)<sub>3</sub>N complexes by reaction with [CyRuCl<sub>2</sub>]<sub>2</sub> suggested that other polypyridyl complexes might be accessible *via* this route and an efficient synthesis of *cis*-di-

chloridobis(2,2'-bipyridyl)ruthenium(II) (**1**) was achieved by the direct reaction of [CyRuCl<sub>2</sub>]<sub>2</sub> with 2,2'-bipyridyl.

## 2. Experimental

### 2.1. Synthesis and crystallization

(2-py)<sub>3</sub>N was synthesized *via* a procedure similar to that of Mosny & Crabtree (1996). *cis*-[RuCl<sub>2</sub>{ $\kappa^2$ -(2-py)<sub>3</sub>N}<sub>2</sub>] (**1**) was prepared by refluxing [CyRuCl<sub>2</sub>]<sub>2</sub> with (2-py)<sub>3</sub>N in diglyme and *cis*-[RuCl<sub>2</sub>{ $\kappa^2$ -(2-py)<sub>3</sub>N}<sub>2</sub>] $\cdot$ CHCl<sub>3</sub> (**1a**) was formed by recrystallization of **1** from chloroform/pentane. Crystallization of **1** from methylene chloride provided [RuCl<sub>2</sub>{ $\kappa^2$ -py<sub>3</sub>N}<sub>2</sub>] $\cdot$ 2CH<sub>2</sub>Cl<sub>2</sub> (**1b**). Treatment of **1a** with AgSbF<sub>6</sub> gave [RuCl{ $\kappa^2$ -(2-py)<sub>3</sub>N}{ $\kappa^3$ -(2-py)<sub>3</sub>N}][SbF<sub>6</sub>] (**2**) as the methylene chloride solvate, **2a**.

Crystallization of **2a** from chloroform provided [RuCl{ $\kappa^2$ -py<sub>3</sub>N}{ $\kappa^3$ -py<sub>3</sub>N}][SbF<sub>6</sub>] $\cdot$ CHCl<sub>3</sub>, **2b**. Treatment of **2** with AgSbF<sub>6</sub> gave [Ru{ $\kappa^3$ -(2-py)<sub>3</sub>N}<sub>2</sub>][SbF<sub>6</sub>] (**3**). Full details of the syntheses are available in the supporting information and the structures of **1b** and **2b** are shown in Scheme 1.

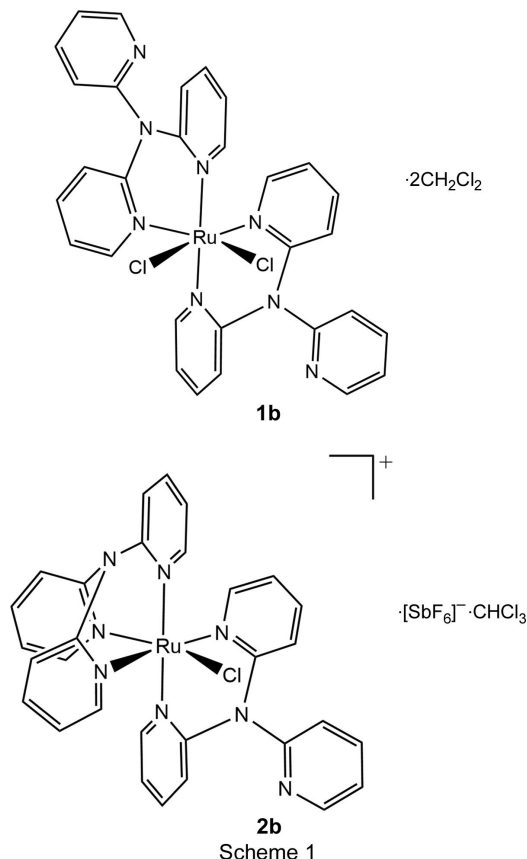
### 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1 and selected metrical parameters are given in Table 2. The full atom-numbering schemes for **1b** and **2b** are shown in Figs. 1 and 2, respectively. H atoms were included in the model at geometrically calculated positions and refined using a riding model. The isotropic

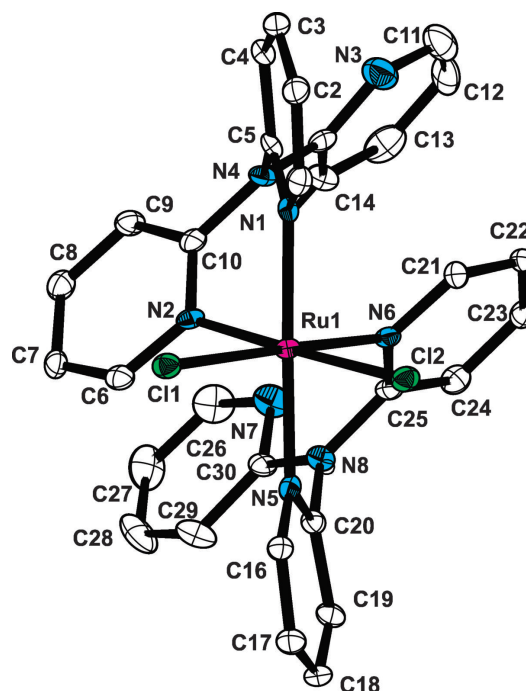
displacement parameters of all H atoms were fixed at 1.2 times the  $U_{eq}$  value of the atoms to which they were linked.

### 3. Results and discussion

The widely-used ruthenium(II) compound  $[\text{CyRuCl}_2]_2$  (Cy = *p*-isopropyltoluene or cymene) is well known to lose cymene when heated with excess hexamethylbenzene to give  $[(\eta^6\text{-C}_6\text{Me}_6)\text{RuCl}_2]_2$  in high yield. A similar result was expected in the reaction of  $[\text{CyRuCl}_2]_2$  with excess (2-py) $_3\text{N}$ . However, the



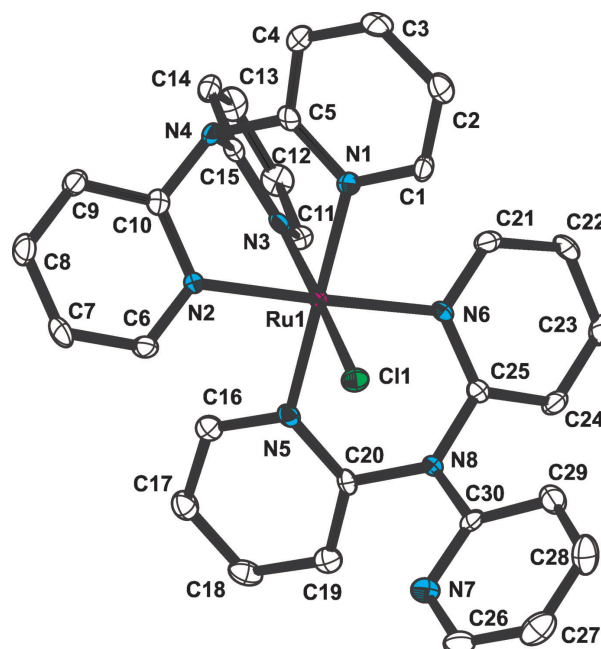
reaction of  $[\text{CyRuCl}_2]_2$  with (2-py) $_3\text{N}$  in refluxing ethylene glycol dimethyl ether (diglyme) followed by recrystallization from chloroform resulted in the isolation of air-stable red *cis*- $[\text{RuCl}_2\{\kappa^2\text{-(2-py)}_3\text{N}\}_2]\cdot\text{CHCl}_3$ , **1a**, in 92% yield. Recrystallization from methylene chloride gave *cis*- $[\text{RuCl}_2\{\kappa^2\text{-(2-py)}_3\text{N}\}_2]\cdot 2\text{CH}_2\text{Cl}_2$ , **1b**. Compound **1b** was characterized by  $^1\text{H}$  NMR spectroscopy, elemental analysis, and X-ray structure determination. For **1b**, the  $^1\text{H}$  NMR spectrum shows 12 chemical shifts for the py $_3\text{N}$  protons consistent with two equivalent  $\kappa^2\text{-py}_3\text{N}$  ligands. Likewise, the  $^{13}\text{C}$  NMR spectrum suggests two equivalent  $\kappa^2\text{-py}_3\text{N}$  ligands having 15 pyridine resonances. The X-ray structure definitively shows a  $\kappa^2\text{-}\kappa^2$  arrangement of the two (2-py) $_3\text{N}$  ligands, with *cis* chloride ligands; however, the unbound pyridines are oriented differently in the two ligands. Assuming that there is a relatively low barrier to rotation about the C–N bonds of the unbound pyridyl group, the conformers would interconvert rapidly on the NMR time scale resulting in equivalence of the two py $_3\text{N}$  ligands in the



**Figure 1**

The complete atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level, for complex **1b**. H atoms are not shown.

NMR spectrum. The complex is chiral and crystallizes as a racemic mixture of enantiomers in a centric space group. The effective planarity about the central N atom in the py $_3\text{N}$  ligands is notable, with N4 being 0.004 Å out of the C5/C10/C15 plane and N8 being 0.005 Å out of the C20/C25/C30 plane.



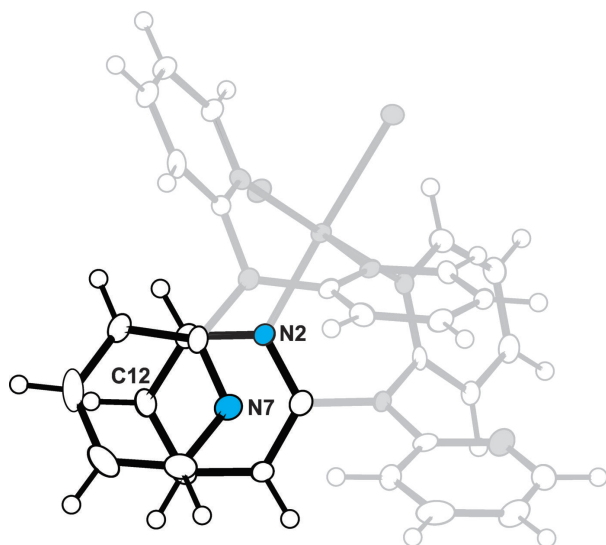
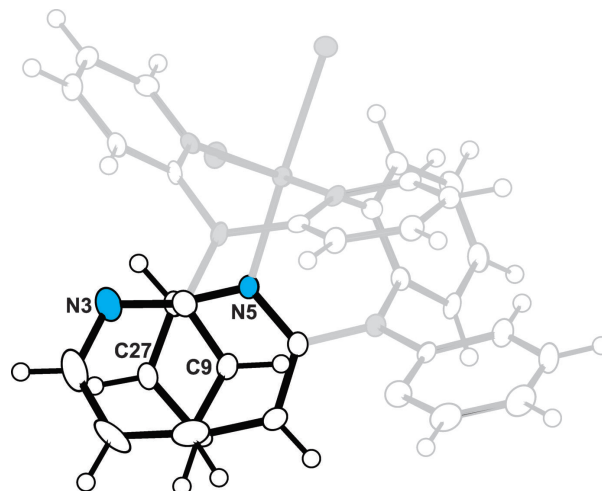
**Figure 2**

The complete atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level, for complex **2b**. H atoms are not shown.

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

	<b>1b</b>	<b>2b</b>
Ru1—C11	2.4157 (9)	2.4269 (9)
Ru1—C12	2.4051 (9)	
Ru1—N1	2.050 (3)	2.057 (3)
Ru1—N2	2.027 (3)	2.065 (3)
Ru1—N3		2.046 (3)
Ru1—N5	2.033 (3)	2.090 (3)
Ru1—N6	2.049 (3)	2.077 (3)
C11—Ru1—C12	91.45 (3)	
C11—Ru1—N1	88.02 (8)	90.16 (9)
C11—Ru1—N2	89.57 (9)	88.41 (9)
C11—Ru1—N3		173.96 (10)
C11—Ru1—N5	91.76 (9)	90.79 (8)
C11—Ru1—N6	178.31 (9)	94.47 (8)
N1—Ru1—N2	86.39 (12)	86.14 (12)
N1—Ru1—N3		85.98 (12)
N1—Ru1—N5	93.48 (14)	178.97 (12)
N1—Ru1—N6	177.86 (12)	93.53 (13)
N2—Ru1—N3		86.69 (12)
N2—Ru1—N5	89.74 (12)	94.29 (12)
N2—Ru1—N6	95.74(11)	177.10 (12)
N3—Ru1—N5		93.11 (12)
N3—Ru1—N6		90.41 (12)
N5—Ru1—N6	86.78 (12)	85.99 (13)
C5—N4—C10	119.8 (3)	111.8 (3)
C5—N4—C15	118.7 (3)	111.2 (3)
C10—N4—C15	121.6 (3)	113.0 (3)
C20—N8—C25	120.7 (3)	117.7 (3)
C20—N8—C30	117.5 (3)	122.1 (3)
C25—N8—C30	121.8 (3)	120.3 (3)

The orientation of the unbound pyridine is controlled by  $\pi$ -stacking, although there are two possible orientations for effective stacking. The distance of the centroid of the free N7-ring to the mean plane of the N2-ring bound to the Ru atom is 3.387 Å. The rings are offset, *i.e.* they are not directly over one another, the N7-ring centroid being almost aligned with atom C12, and the N atom is almost aligned with the centroid of the N2-ring, as shown in Fig. 3. This implies an angle of 21° between the ring normal and the centroid-to-centroid vector,

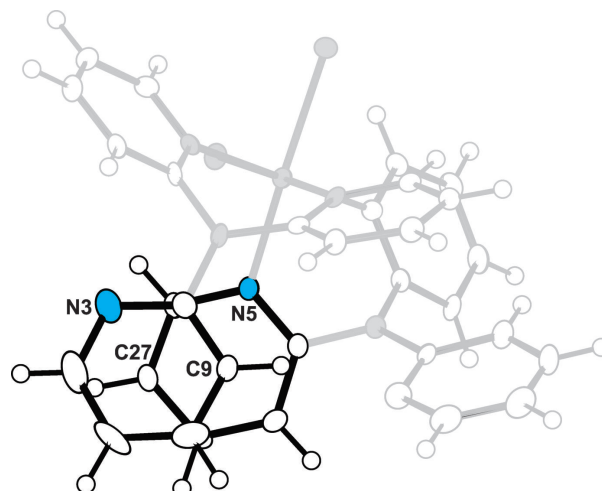

**Figure 3**  
 $\pi$ -stacking of the N2- and N7-containing rings in **1b**.

**Figure 4**  
 The offset  $\pi$ -stacking between rings in **1b**. Portions of the other pyridine rings have been removed so that the view of the interaction is not obscured.

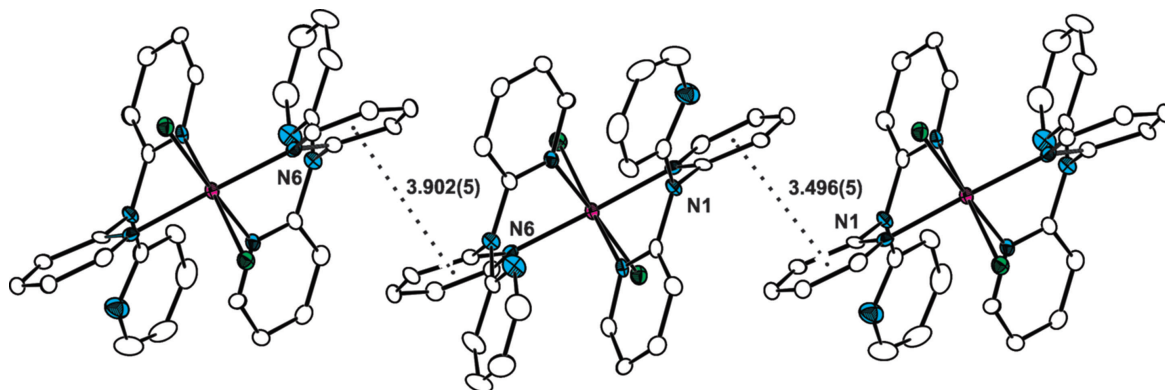
and a shift of one ring with respect to the other of 1.27 Å, as shown in Fig. 4. Offset stacking is the most common mode of  $\pi$ -stacking found for nitrogen-containing aromatics and centroid–centroid separations of less than 3.6 Å are considered fairly strong interactions, although the strongest known have centroid–centroid separations of  $\sim$ 3.4 Å (Janiak, 2000). A  $\sim$ 20° angle between the ring normal and the the centroid-to-centroid vector is also rather typical (Janiak, 2000).

The pyridine ring containing atom N3 is nearly parallel to the Ru-bound N5 pyridine ring with distances of approach between 3.13 and 3.56 Å to the plane of the N5 pyridine ring and a centroid-to-centroid distance of 3.568 Å. The distance from the N3-ring centroid to the mean N5-ring plane is 3.347 Å.

Again, the rings are offset, however, atom N3 is not directly over the N5-ring and atom C9 is directly over the centroid of the N5-ring, as shown in Fig. 5.

Furthermore, there are weak intermolecular  $\pi$ -stacking interactions between the pyridyl rings that are *trans* to each


**Figure 5**  
 $\pi$ -stacking of the N3- and N5-containing rings in **1b**.



**Figure 6**  
Intermolecular  $\pi$ -stacking in **1b** (distances in Å).

other (Fig. 6). The N1 pyridyl rings in one molecule interact with adjacent N1 pyridyl rings (centroid-to-centroid distance = 3.496 Å) and the N6 pyridyl rings interact with adjacent N6 pyridyl rings (centroid-to-centroid distance = 3.902 Å) with slipped overlap to form a chain owing to the interaction between *trans*-pyridine rings.

Examination of the structure reveals that the unbound pyridine rings in the complex appear to be close enough to each other to allow **1b** to act as a chiral bidentate ligand by coordination to another metal atom through the unbound N-atom donors. There is considerable interest in bimetallic and multimetallic polypyridyl complexes, and **1b** could be an effective reagent in the formation of such complexes.

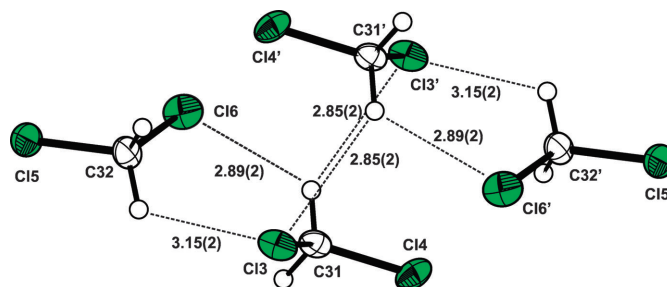
Another interesting feature of this structure is that the complexes are arranged in a manner that forms a cavity which contains two hydrogen-bonded dimers of methylene chloride molecules, with a C31—H···Cl6 hydrogen bond of 2.89 Å, which is in the range observed for other C—H···Cl hydrogen bonds (Thallapally & Nangia, 2001; Freytag & Jones, 2000; Neve *et al.*, 2002). Furthermore, the dimers are close to their symmetry-related equivalents and there is even a shorter C31—H···Cl3' hydrogen bond and its counterpart, which leads to the formation of a tetramer; this is shown in Fig. 7. Since the distance measured in the X-ray data overestimates the separation as the actual C—H bond distance is longer than the value of 0.99 Å used in the riding model, these are relatively strong bonds. Normally one would expect any hydrogen bonding involving methylene chloride to occur with one of the free pyridine N atoms; however, in this case, pyridines are involved in  $\pi$ -stacking and this produces orientations in which the lone pairs are not sterically accessible.

When **1a** was treated with slightly more than one equivalent of silver(I) hexafluoroantimonate in methylene chloride, it yielded an air-stable yellow  $\kappa^3$ - $\kappa^2$  complex  $[\text{RuCl}\{\kappa^2\text{-py}_3\text{N}\}\{\kappa^3\text{-py}_3\text{N}\}][\text{SbF}_6]\cdot\text{CH}_2\text{Cl}_2$ , **2a**, in 73% yield. Complex **2a** was characterized by  $^1\text{H}$  NMR spectroscopy and elemental analysis. Crystallization from chloroform yielded  $[\text{RuCl}\{\kappa^2\text{-(2-py)}_3\text{N}\}\{\kappa^3\text{-(2-py)}_3\text{N}\}][\text{SbF}_6]\cdot\text{CHCl}_3$ , **2b**, and the structure is shown in Fig. 2. This complex represents, to our knowledge, the first example of a  $\kappa^2, \kappa^3$ -(2-py)<sub>3</sub>N complex.

Table 2 shows that in **2b** the average C—N4—C angle is 112° and the central N atom is pyramidal (0.42 Å out of the

C5/C10/C15 plane), whereas the average C—N8—C angle is 120.0° and the central N atom is essentially in the plane (0.006 Å out of the C20/C25/C30 plane). This demonstrates the proclivity of the central N atom in (2-py)<sub>3</sub>N to be  $sp^2$ -hybridized and provide some added stability to a  $\kappa^2$ -(2-py)<sub>3</sub>N mode of binding. In the  $\kappa^3$  mode of (2-py)<sub>3</sub>N, the N—Ru—N angles are all compressed to less than 90°, having values of 86.14 (12), 85.98 (12), and 86.69 (12)° for N1—Ru—N2, N1—Ru—N3, and N2—Ru—N3, respectively. The bidentate portion of the  $\kappa^2$ -mode of (2-py)<sub>3</sub>N shows an even smaller angle of 85.99 (13)° for N5—Ru—N6. Hydrogen bonding of the solvent, *i.e.* CHCl<sub>3</sub>, is hydrogen bonded to the chloride ligand attached to the Ru atom (C—H···Cl—Ru = 2.72 Å). This is substantially closer than the nearest approach of the pyridine C6—H group to Cl—Ru of 2.93 Å, which is only slightly shorter than the sum of the van der Waals radii (2.95 Å).

Treatment of **2** with an excess of silver(I) hexafluoroantimonate gives the bright-yellow air-stable complex  $[\text{Ru}\{\kappa^3\text{-py}_3\text{N}\}_2][\text{SbF}_6]_2$ , **3**, in 68% yield. This cation has been prepared previously by Keene and co-workers from  $[\text{Ru}(\text{DMF})_6]^{2+}$  (DMF is dimethylformamide) and excess (2-py)<sub>3</sub>N, and isolated as the hexafluoridophosphate (Keene *et al.*, 1988a). The reaction of  $[\text{CyRuCl}_2]_2$  with (2-py)<sub>3</sub>N in methylene chloride followed by treatment with excess sodium hexafluoroantimonate in acetone gives  $[\text{CyRuCl}\{\kappa^2\text{-(2-py)}_3\text{N}\}][\text{SbF}_6]$ , **4**, in 95% yield. This complex was prepared previously and characterized crystallographically by Crabtree and Mosny (Mosny *et al.*, 1995) in lower yield by reaction of  $[\text{CyRuCl}_2]_2$  with one



**Figure 7**  
The methylene chloride hydrogen-bonded tetramer (H···Cl distances in Å). The primed atoms are related by a center of inversion.

equivalent of silver(I) hexafluoroantimonate in the presence of (2-py)<sub>3</sub>N. They also reported the preparation of the complex [CyRu{κ<sup>3</sup>-(2-py)<sub>3</sub>N}][SbF<sub>6</sub>]<sub>2</sub> by reaction of **4** with silver(I) hexafluoroantimonate.

Capitalizing upon the relative ease of preparation of these κ<sup>2</sup>-(2-py)<sub>3</sub>N complexes from readily available [CyRuCl<sub>2</sub>]<sub>2</sub>, a successful synthesis of [RuCl<sub>2</sub>(2,2'-bipy)<sub>2</sub>], **5**, was achieved by treating [CyRuCl<sub>2</sub>]<sub>2</sub> with excess 2,2'-bipyridine in diglyme under reflux. This route to **5** is efficient and may in some cases be preferred over existing literature syntheses.

#### 4. Conclusions

We have found that [CyRuCl<sub>2</sub>]<sub>2</sub> is an effective precursor for the preparation of κ<sup>2</sup>-(2-py)<sub>3</sub>N and κ<sup>3</sup>-(2-py)<sub>3</sub>N complexes of ruthenium. To our knowledge, the use of [CyRuCl<sub>2</sub>]<sub>2</sub> in the preparation of polypyridyl ruthenium complexes is unprecedented, and this may be a general route in the preparation of many other *cis*-RuCl<sub>2</sub>L<sub>2</sub> complexes (*L* is a bidentate pyridine ligand). This easily prepared precursor allowed the preparation of [RuCl{κ<sup>2</sup>-(2-py)<sub>3</sub>N}{κ<sup>3</sup>-(2-py)<sub>3</sub>N}][SbF<sub>6</sub>]·CHCl<sub>3</sub>, which is the first example of a complex containing both a κ<sup>2</sup>-(2-py)<sub>3</sub>N and a κ<sup>3</sup>-(2-py)<sub>3</sub>N ligand. The neutral *cis*-[RuCl<sub>2</sub>{κ<sup>2</sup>-(2-py)<sub>3</sub>N}<sub>2</sub>]-CH<sub>2</sub>Cl<sub>2</sub> complex exhibited multiple modes of π-stacking between the ligands both intramolecularly and intermolecularly, and also contains a hydrogen-bonded tetramer of methylene chloride.

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## supporting information

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## Studies of $\kappa^2$ - and $\kappa^3$ -tripyridylamine complexes of ruthenium and $\pi$ -stacking by pyridyls

**Jack Faller, Kevin J. Chase, Jonathan Parr and Brandon Mercado**

### Computing details

#### Dichloridobis[tris(pyridin-2-yl)amine- $\kappa^2N,N'$ ]ruthenium(II) dichloromethane disolvate (1b)

##### Crystal data

[RuCl<sub>2</sub>(C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>)<sub>2</sub>] $\cdot$ 2CH<sub>2</sub>Cl<sub>2</sub>

$M_r$  = 838.39

Triclinic,  $P\bar{1}$

$a$  = 11.2435 (7) Å

$b$  = 11.4038 (7) Å

$c$  = 13.6340 (7) Å

$\alpha$  = 74.278 (5)°

$\beta$  = 75.995 (5)°

$\gamma$  = 84.642 (5)°

$V$  = 1631.99 (17) Å<sup>3</sup>

$Z$  = 2

$F(000)$  = 844

$D_x$  = 1.706 Mg m<sup>-3</sup>

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

Cell parameters from 15256 reflections

$\theta$  = 2.8–30.5°

$\mu$  = 1.01 mm<sup>-1</sup>

$T$  = 93 K

Prism, orange

0.37 × 0.29 × 0.2 mm

##### Data collection

Rigaku Mercury275R CCD  
diffractometer

Detector resolution: 6.8 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan  
(CrysAlis PRO; Rigaku OD, 2019)

$T_{\min}$  = 0.926,  $T_{\max}$  = 1.000

34353 measured reflections

9877 independent reflections

6726 reflections with  $I > 2\sigma(I)$

$R_{\text{int}}$  = 0.093

$\theta_{\max}$  = 30.5°,  $\theta_{\min}$  = 2.7°

$h$  = -15→16

$k$  = -16→16

$l$  = -19→19

##### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$  = 0.061

$wR(F^2)$  = 0.108

$S$  = 1.03

9877 reflections

424 parameters

0 restraints

Primary atom site location: dual

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 3.9087P]$

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

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

$\Delta\rho_{\max}$  = 0.97 e Å<sup>-3</sup>

$\Delta\rho_{\min}$  = -0.76 e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ru1	0.76400 (3)	0.73839 (3)	0.50380 (2)	0.01125 (8)
C11	0.96002 (8)	0.71921 (8)	0.38718 (7)	0.01494 (18)
C12	0.66580 (8)	0.80970 (8)	0.35919 (7)	0.01553 (19)
C13	1.14367 (11)	0.95770 (11)	0.88069 (9)	0.0323 (3)
C14	0.89342 (11)	0.99325 (10)	0.85424 (9)	0.0312 (3)
C15	1.37129 (11)	1.34020 (11)	0.86258 (9)	0.0361 (3)
C16	1.10635 (11)	1.32412 (11)	0.92797 (9)	0.0358 (3)
N1	0.8092 (3)	0.9115 (3)	0.4951 (2)	0.0123 (6)
N2	0.8448 (3)	0.6834 (3)	0.6271 (2)	0.0123 (6)
N3	0.6383 (3)	1.0142 (3)	0.7273 (3)	0.0257 (8)
N4	0.7763 (3)	0.8649 (3)	0.6766 (2)	0.0127 (6)
N5	0.5991 (3)	0.7491 (3)	0.6038 (2)	0.0122 (6)
N6	0.7166 (3)	0.5678 (3)	0.5075 (2)	0.0123 (6)
N7	0.6217 (3)	0.5179 (3)	0.8553 (3)	0.0220 (7)
N8	0.6141 (3)	0.5413 (3)	0.6825 (2)	0.0140 (6)
C1	0.8431 (3)	0.9909 (3)	0.4010 (3)	0.0158 (8)
H1	0.841044	0.966068	0.340388	0.019*
C2	0.8801 (3)	1.1051 (3)	0.3888 (3)	0.0162 (8)
H2	0.899673	1.159809	0.321172	0.019*
C3	0.8888 (3)	1.1405 (3)	0.4754 (3)	0.0179 (8)
H3	0.916364	1.219205	0.468523	0.021*
C4	0.8571 (3)	1.0602 (3)	0.5717 (3)	0.0146 (7)
H4	0.863908	1.081662	0.632727	0.017*
C5	0.8150 (3)	0.9472 (3)	0.5787 (3)	0.0129 (7)
C6	0.5434 (4)	1.0466 (4)	0.7950 (4)	0.0316 (11)
H6	0.512007	1.128064	0.778063	0.038*
C7	0.4882 (4)	0.9701 (5)	0.8872 (4)	0.0311 (11)
H7	0.420620	0.997012	0.933752	0.037*
C8	0.5344 (4)	0.8523 (4)	0.9101 (3)	0.0277 (10)
H8	0.498303	0.796129	0.973571	0.033*
C9	0.6313 (4)	0.8157 (3)	0.8427 (3)	0.0176 (8)
H9	0.664006	0.734654	0.858153	0.021*
C10	0.6803 (3)	0.8989 (3)	0.7520 (3)	0.0156 (8)
C11	0.9096 (3)	0.5772 (3)	0.6425 (3)	0.0146 (7)
H11	0.921410	0.531855	0.591715	0.017*
C12	0.9591 (3)	0.5317 (3)	0.7280 (3)	0.0161 (8)
H12	1.001666	0.454927	0.737285	0.019*
C13	0.9465 (3)	0.5987 (3)	0.8004 (3)	0.0175 (8)
H13	0.979346	0.568807	0.860782	0.021*



C14	0.8857 (3)	0.7091 (3)	0.7833 (3)	0.0158 (8)
H14	0.877527	0.757892	0.831152	0.019*
C15	0.8363 (3)	0.7496 (3)	0.6970 (3)	0.0137 (7)
C16	0.7464 (3)	0.5277 (3)	0.4209 (3)	0.0144 (7)
H16	0.797867	0.575801	0.360192	0.017*
C17	0.7062 (3)	0.4205 (3)	0.4161 (3)	0.0176 (8)
H17	0.733441	0.392770	0.354419	0.021*
C18	0.6264 (3)	0.3535 (3)	0.5008 (3)	0.0184 (8)
H18	0.595363	0.280010	0.498074	0.022*
C19	0.5921 (3)	0.3942 (3)	0.5895 (3)	0.0170 (8)
H19	0.535170	0.350752	0.648962	0.020*
C20	0.6420 (3)	0.5000 (3)	0.5910 (3)	0.0128 (7)
C21	0.6584 (4)	0.4546 (4)	0.9414 (3)	0.0267 (10)
H21	0.639614	0.487612	1.000517	0.032*
C22	0.7203 (4)	0.3469 (4)	0.9493 (3)	0.0298 (10)
H22	0.745311	0.305038	1.011724	0.036*
C23	0.7458 (4)	0.2998 (4)	0.8640 (4)	0.0311 (11)
H23	0.788795	0.223605	0.867265	0.037*
C24	0.7103 (4)	0.3607 (3)	0.7744 (3)	0.0226 (9)
H24	0.727817	0.328566	0.714851	0.027*
C25	0.6479 (3)	0.4713 (3)	0.7736 (3)	0.0146 (7)
C26	0.5354 (3)	0.8562 (3)	0.5945 (3)	0.0149 (7)
H26	0.567244	0.923808	0.538769	0.018*
C27	0.4275 (3)	0.8713 (3)	0.6615 (3)	0.0147 (7)
H27	0.386480	0.948849	0.654234	0.018*
C28	0.3784 (3)	0.7724 (4)	0.7402 (3)	0.0169 (8)
H28	0.302883	0.780619	0.787888	0.020*
C29	0.4402 (3)	0.6625 (3)	0.7484 (3)	0.0165 (8)
H29	0.407755	0.592811	0.801363	0.020*
C30	0.5503 (3)	0.6541 (3)	0.6789 (3)	0.0134 (7)
C31	1.0237 (4)	1.0647 (4)	0.8564 (3)	0.0245 (9)
H31A	1.002534	1.109425	0.911565	0.029*
H31B	1.051384	1.124580	0.788381	0.029*
C32	1.2459 (4)	1.2483 (4)	0.8893 (4)	0.0278 (10)
H32A	1.254901	1.174403	0.945609	0.033*
H32B	1.244774	1.221948	0.826080	0.033*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ru1	0.01253 (15)	0.01005 (15)	0.01226 (14)	-0.00182 (11)	-0.00308 (11)	-0.00394 (11)
Cl1	0.0144 (4)	0.0150 (4)	0.0155 (4)	-0.0022 (3)	-0.0007 (3)	-0.0060 (4)
Cl2	0.0191 (5)	0.0143 (4)	0.0156 (4)	-0.0009 (4)	-0.0076 (4)	-0.0044 (4)
Cl3	0.0353 (6)	0.0345 (6)	0.0242 (5)	0.0071 (5)	-0.0049 (5)	-0.0069 (5)
Cl4	0.0423 (7)	0.0231 (5)	0.0348 (6)	-0.0018 (5)	-0.0160 (5)	-0.0119 (5)
Cl5	0.0419 (7)	0.0314 (6)	0.0354 (6)	-0.0143 (5)	0.0000 (5)	-0.0127 (5)
Cl6	0.0376 (7)	0.0344 (6)	0.0377 (7)	0.0091 (5)	-0.0129 (5)	-0.0126 (5)
N1	0.0091 (14)	0.0130 (15)	0.0152 (15)	0.0023 (12)	-0.0031 (12)	-0.0051 (12)

N2	0.0139 (15)	0.0094 (15)	0.0134 (15)	-0.0048 (12)	-0.0025 (12)	-0.0017 (12)
N3	0.031 (2)	0.0227 (19)	0.028 (2)	0.0054 (16)	-0.0105 (16)	-0.0126 (16)
N4	0.0179 (16)	0.0076 (14)	0.0134 (15)	-0.0005 (12)	-0.0052 (12)	-0.0027 (12)
N5	0.0143 (15)	0.0110 (15)	0.0139 (15)	-0.0011 (12)	-0.0056 (12)	-0.0052 (12)
N6	0.0101 (14)	0.0137 (15)	0.0132 (15)	-0.0004 (12)	-0.0042 (12)	-0.0024 (12)
N7	0.0280 (19)	0.0210 (18)	0.0160 (17)	-0.0002 (15)	-0.0027 (14)	-0.0053 (14)
N8	0.0167 (16)	0.0121 (15)	0.0132 (15)	-0.0002 (12)	-0.0031 (12)	-0.0033 (12)
C1	0.0127 (18)	0.019 (2)	0.0152 (18)	-0.0004 (15)	-0.0025 (14)	-0.0045 (15)
C2	0.0139 (18)	0.0140 (19)	0.0193 (19)	-0.0021 (15)	-0.0034 (15)	-0.0013 (15)
C3	0.0147 (19)	0.0114 (18)	0.029 (2)	-0.0012 (15)	-0.0070 (16)	-0.0046 (16)
C4	0.0135 (18)	0.0124 (18)	0.0188 (19)	0.0030 (14)	-0.0052 (15)	-0.0055 (15)
C5	0.0128 (17)	0.0086 (17)	0.0171 (18)	0.0042 (14)	-0.0054 (14)	-0.0027 (14)
C6	0.041 (3)	0.030 (3)	0.034 (3)	0.017 (2)	-0.024 (2)	-0.017 (2)
C7	0.019 (2)	0.048 (3)	0.036 (3)	0.013 (2)	-0.0082 (19)	-0.030 (2)
C8	0.028 (2)	0.038 (3)	0.018 (2)	-0.012 (2)	-0.0026 (18)	-0.0089 (19)
C9	0.022 (2)	0.0124 (18)	0.0183 (19)	0.0001 (15)	-0.0044 (16)	-0.0037 (15)
C10	0.0164 (19)	0.0178 (19)	0.0180 (19)	-0.0015 (15)	-0.0076 (15)	-0.0099 (16)
C11	0.0139 (18)	0.0129 (18)	0.0156 (18)	-0.0039 (14)	0.0005 (14)	-0.0036 (15)
C12	0.0102 (17)	0.0145 (19)	0.022 (2)	-0.0006 (14)	-0.0037 (15)	-0.0021 (16)
C13	0.0169 (19)	0.018 (2)	0.0179 (19)	-0.0015 (15)	-0.0069 (15)	-0.0030 (16)
C14	0.0204 (19)	0.0144 (19)	0.0148 (18)	-0.0006 (15)	-0.0067 (15)	-0.0050 (15)
C15	0.0106 (17)	0.0125 (18)	0.0164 (18)	-0.0049 (14)	0.0010 (14)	-0.0031 (14)
C16	0.0133 (18)	0.0145 (19)	0.0175 (18)	0.0002 (14)	-0.0039 (14)	-0.0072 (15)
C17	0.019 (2)	0.017 (2)	0.0202 (19)	0.0012 (16)	-0.0066 (16)	-0.0095 (16)
C18	0.0175 (19)	0.0128 (19)	0.030 (2)	-0.0005 (15)	-0.0096 (17)	-0.0097 (17)
C19	0.0183 (19)	0.0081 (17)	0.023 (2)	-0.0010 (15)	-0.0058 (16)	0.0001 (15)
C20	0.0145 (18)	0.0115 (18)	0.0137 (17)	0.0014 (14)	-0.0055 (14)	-0.0039 (14)
C21	0.035 (2)	0.029 (2)	0.014 (2)	-0.003 (2)	-0.0041 (18)	-0.0036 (18)
C22	0.031 (2)	0.032 (3)	0.022 (2)	0.001 (2)	-0.0104 (19)	0.0049 (19)
C23	0.030 (2)	0.015 (2)	0.038 (3)	0.0063 (18)	-0.001 (2)	0.0024 (19)
C24	0.034 (2)	0.0125 (19)	0.020 (2)	0.0003 (17)	-0.0021 (18)	-0.0043 (16)
C25	0.0143 (18)	0.0088 (17)	0.0184 (19)	-0.0028 (14)	-0.0009 (15)	-0.0013 (14)
C26	0.0146 (18)	0.0136 (18)	0.0180 (19)	0.0018 (15)	-0.0073 (15)	-0.0041 (15)
C27	0.0170 (19)	0.0127 (18)	0.0177 (18)	0.0023 (15)	-0.0080 (15)	-0.0067 (15)
C28	0.0122 (18)	0.022 (2)	0.0195 (19)	-0.0004 (15)	-0.0028 (15)	-0.0107 (16)
C29	0.0170 (19)	0.0170 (19)	0.0147 (18)	-0.0039 (15)	-0.0036 (15)	-0.0014 (15)
C30	0.0160 (18)	0.0113 (18)	0.0156 (18)	-0.0007 (14)	-0.0054 (14)	-0.0060 (15)
C31	0.031 (2)	0.018 (2)	0.023 (2)	0.0005 (18)	-0.0010 (18)	-0.0079 (17)
C32	0.030 (2)	0.020 (2)	0.031 (2)	-0.0055 (18)	0.0015 (19)	-0.0092 (19)

*Geometric parameters (Å, °)*

Ru1—C11	2.4157 (9)	C8—H8	0.9500
Ru1—C12	2.4051 (9)	C8—C9	1.358 (6)
Ru1—N1	2.050 (3)	C9—H9	0.9500
Ru1—N2	2.027 (3)	C9—C10	1.365 (5)
Ru1—N5	2.033 (3)	C11—H11	0.9500
Ru1—N6	2.049 (3)	C11—C12	1.367 (5)

C13—C31	1.763 (4)	C12—H12	0.9500
C14—C31	1.752 (4)	C12—C13	1.378 (5)
C15—C32	1.744 (4)	C13—H13	0.9500
C16—C32	1.755 (4)	C13—C14	1.366 (5)
N1—C1	1.345 (5)	C14—H14	0.9500
N1—C5	1.327 (4)	C14—C15	1.370 (5)
N2—C11	1.346 (5)	C16—H16	0.9500
N2—C15	1.348 (4)	C16—C17	1.365 (5)
N3—C6	1.327 (6)	C17—H17	0.9500
N3—C10	1.337 (5)	C17—C18	1.368 (5)
N4—C5	1.403 (5)	C18—H18	0.9500
N4—C10	1.406 (5)	C18—C19	1.369 (5)
N4—C15	1.410 (5)	C19—H19	0.9500
N5—C26	1.348 (5)	C19—C20	1.384 (5)
N5—C30	1.327 (5)	C21—H21	0.9500
N6—C16	1.336 (4)	C21—C22	1.345 (6)
N6—C20	1.335 (5)	C22—H22	0.9500
N7—C21	1.338 (5)	C22—C23	1.367 (6)
N7—C25	1.320 (5)	C23—H23	0.9500
N8—C20	1.406 (4)	C23—C24	1.363 (6)
N8—C25	1.399 (5)	C24—H24	0.9500
N8—C30	1.408 (5)	C24—C25	1.384 (5)
C1—H1	0.9500	C26—H26	0.9500
C1—C2	1.359 (5)	C26—C27	1.359 (5)
C2—H2	0.9500	C27—H27	0.9500
C2—C3	1.374 (5)	C27—C28	1.379 (5)
C3—H3	0.9500	C28—H28	0.9500
C3—C4	1.368 (5)	C28—C29	1.366 (5)
C4—H4	0.9500	C29—H29	0.9500
C4—C5	1.386 (5)	C29—C30	1.378 (5)
C6—H6	0.9500	C31—H31A	0.9900
C6—C7	1.362 (7)	C31—H31B	0.9900
C7—H7	0.9500	C32—H32A	0.9900
C7—C8	1.376 (6)	C32—H32B	0.9900
Cl2—Ru1—Cl1	91.45 (3)	C11—C12—C13	119.1 (4)
N1—Ru1—Cl1	88.02 (8)	C13—C12—H12	120.5
N1—Ru1—Cl2	92.07 (9)	C12—C13—H13	120.8
N2—Ru1—Cl1	89.57 (9)	C14—C13—C12	118.4 (3)
N2—Ru1—Cl2	178.12 (9)	C14—C13—H13	120.8
N2—Ru1—N1	86.39 (12)	C13—C14—H14	120.0
N2—Ru1—N5	89.74 (12)	C13—C14—C15	120.0 (3)
N2—Ru1—N6	95.74 (11)	C15—C14—H14	120.0
N5—Ru1—Cl1	178.31 (9)	N2—C15—N4	117.1 (3)
N5—Ru1—Cl2	89.28 (9)	N2—C15—C14	122.2 (3)
N5—Ru1—N1	93.48 (12)	C14—C15—N4	120.7 (3)
N5—Ru1—N6	86.78 (12)	N6—C16—H16	118.6
N6—Ru1—Cl1	91.76 (9)	N6—C16—C17	122.8 (4)

N6—Ru1—C12	85.81 (8)	C17—C16—H16	118.6
N6—Ru1—N1	177.86 (12)	C16—C17—H17	120.3
C1—N1—Ru1	119.7 (2)	C16—C17—C18	119.4 (4)
C5—N1—Ru1	122.6 (2)	C18—C17—H17	120.3
C5—N1—C1	117.5 (3)	C17—C18—H18	120.6
C11—N2—Ru1	120.5 (2)	C17—C18—C19	118.7 (3)
C11—N2—C15	117.2 (3)	C19—C18—H18	120.6
C15—N2—Ru1	122.4 (2)	C18—C19—H19	120.6
C6—N3—C10	117.1 (4)	C18—C19—C20	118.7 (4)
C5—N4—C10	119.8 (3)	C20—C19—H19	120.6
C5—N4—C15	118.7 (3)	N6—C20—N8	116.9 (3)
C10—N4—C15	121.6 (3)	N6—C20—C19	122.6 (3)
C26—N5—Ru1	119.6 (2)	C19—C20—N8	120.4 (3)
C30—N5—Ru1	122.6 (2)	N7—C21—H21	118.1
C30—N5—C26	117.8 (3)	N7—C21—C22	123.8 (4)
C16—N6—Ru1	120.4 (2)	C22—C21—H21	118.1
C20—N6—Ru1	121.6 (2)	C21—C22—H22	121.2
C20—N6—C16	117.5 (3)	C21—C22—C23	117.5 (4)
C25—N7—C21	117.7 (4)	C23—C22—H22	121.2
C20—N8—C30	117.5 (3)	C22—C23—H23	119.5
C25—N8—C20	120.7 (3)	C24—C23—C22	120.9 (4)
C25—N8—C30	121.8 (3)	C24—C23—H23	119.5
N1—C1—H1	118.5	C23—C24—H24	121.3
N1—C1—C2	123.0 (3)	C23—C24—C25	117.3 (4)
C2—C1—H1	118.5	C25—C24—H24	121.3
C1—C2—H2	120.4	N7—C25—N8	117.1 (3)
C1—C2—C3	119.1 (4)	N7—C25—C24	122.7 (4)
C3—C2—H2	120.4	C24—C25—N8	120.2 (3)
C2—C3—H3	120.6	N5—C26—H26	118.6
C4—C3—C2	118.8 (3)	N5—C26—C27	122.7 (4)
C4—C3—H3	120.6	C27—C26—H26	118.6
C3—C4—H4	120.5	C26—C27—H27	120.5
C3—C4—C5	118.9 (3)	C26—C27—C28	119.0 (3)
C5—C4—H4	120.5	C28—C27—H27	120.5
N1—C5—N4	117.1 (3)	C27—C28—H28	120.6
N1—C5—C4	122.5 (3)	C29—C28—C27	118.8 (4)
C4—C5—N4	120.4 (3)	C29—C28—H28	120.6
N3—C6—H6	118.0	C28—C29—H29	120.4
N3—C6—C7	124.0 (4)	C28—C29—C30	119.2 (4)
C7—C6—H6	118.0	C30—C29—H29	120.4
C6—C7—H7	121.4	N5—C30—N8	116.8 (3)
C6—C7—C8	117.2 (4)	N5—C30—C29	122.5 (3)
C8—C7—H7	121.4	C29—C30—N8	120.6 (3)
C7—C8—H8	119.7	C13—C31—H31A	109.4
C9—C8—C7	120.5 (4)	C13—C31—H31B	109.4
C9—C8—H8	119.7	C14—C31—C13	111.2 (2)
C8—C9—H9	121.0	C14—C31—H31A	109.4
C8—C9—C10	118.0 (4)	C14—C31—H31B	109.4

C10—C9—H9	121.0	H31A—C31—H31B	108.0
N3—C10—N4	116.1 (3)	C15—C32—C16	112.2 (2)
N3—C10—C9	123.2 (4)	C15—C32—H32A	109.2
C9—C10—N4	120.7 (3)	C15—C32—H32B	109.2
N2—C11—H11	118.5	C16—C32—H32A	109.2
N2—C11—C12	123.0 (3)	C16—C32—H32B	109.2
C12—C11—H11	118.5	H32A—C32—H32B	107.9
C11—C12—H12	120.5		
Ru1—N1—C1—C2	-176.7 (3)	C11—C12—C13—C14	-0.6 (5)
Ru1—N1—C5—N4	-6.5 (4)	C12—C13—C14—C15	1.5 (6)
Ru1—N1—C5—C4	173.5 (3)	C13—C14—C15—N2	0.4 (6)
Ru1—N2—C11—C12	-175.5 (3)	C13—C14—C15—N4	-178.2 (3)
Ru1—N2—C15—N4	-4.9 (4)	C15—N2—C11—C12	4.2 (5)
Ru1—N2—C15—C14	176.5 (3)	C15—N4—C5—N1	59.2 (4)
Ru1—N5—C26—C27	-176.9 (3)	C15—N4—C5—C4	-120.8 (4)
Ru1—N5—C30—N8	-4.2 (4)	C15—N4—C10—N3	174.0 (3)
Ru1—N5—C30—C29	178.0 (3)	C15—N4—C10—C9	-8.6 (5)
Ru1—N6—C16—C17	-172.9 (3)	C16—N6—C20—N8	178.2 (3)
Ru1—N6—C20—N8	-10.5 (4)	C16—N6—C20—C19	-2.5 (5)
Ru1—N6—C20—C19	168.8 (3)	C16—C17—C18—C19	-2.0 (6)
N1—C1—C2—C3	2.9 (6)	C17—C18—C19—C20	-1.7 (6)
N2—C11—C12—C13	-2.3 (5)	C18—C19—C20—N6	4.1 (6)
N3—C6—C7—C8	-0.4 (7)	C18—C19—C20—N8	-176.6 (3)
N5—C26—C27—C28	-2.4 (5)	C20—N6—C16—C17	-1.5 (5)
N6—C16—C17—C18	3.8 (6)	C20—N8—C25—N7	178.0 (3)
N7—C21—C22—C23	-0.6 (7)	C20—N8—C25—C24	0.6 (5)
C1—N1—C5—N4	178.3 (3)	C20—N8—C30—N5	-54.5 (4)
C1—N1—C5—C4	-1.7 (5)	C20—N8—C30—C29	123.2 (4)
C1—C2—C3—C4	-1.5 (6)	C21—N7—C25—N8	-177.0 (3)
C2—C3—C4—C5	-1.3 (5)	C21—N7—C25—C24	0.3 (6)
C3—C4—C5—N1	3.0 (5)	C21—C22—C23—C24	0.5 (7)
C3—C4—C5—N4	-177.0 (3)	C22—C23—C24—C25	0.0 (6)
C5—N1—C1—C2	-1.3 (5)	C23—C24—C25—N7	-0.4 (6)
C5—N4—C10—N3	-5.4 (5)	C23—C24—C25—N8	176.9 (4)
C5—N4—C10—C9	172.0 (3)	C25—N7—C21—C22	0.2 (6)
C5—N4—C15—N2	-52.7 (4)	C25—N8—C20—N6	-117.6 (4)
C5—N4—C15—C14	125.9 (4)	C25—N8—C20—C19	63.0 (5)
C6—N3—C10—N4	176.5 (3)	C25—N8—C30—N5	126.2 (4)
C6—N3—C10—C9	-0.8 (6)	C25—N8—C30—C29	-56.1 (5)
C6—C7—C8—C9	0.2 (6)	C26—N5—C30—N8	175.6 (3)
C7—C8—C9—C10	-0.3 (6)	C26—N5—C30—C29	-2.1 (5)
C8—C9—C10—N3	0.7 (6)	C26—C27—C28—C29	0.2 (5)
C8—C9—C10—N4	-176.6 (3)	C27—C28—C29—C30	0.8 (5)
C10—N3—C6—C7	0.7 (6)	C28—C29—C30—N5	0.1 (5)
C10—N4—C5—N1	-121.4 (4)	C28—C29—C30—N8	-177.6 (3)
C10—N4—C5—C4	58.6 (5)	C30—N5—C26—C27	3.3 (5)
C10—N4—C15—N2	127.9 (3)	C30—N8—C20—N6	63.1 (4)

C10—N4—C15—C14	−53.5 (5)	C30—N8—C20—C19	−116.3 (4)
C11—N2—C15—N4	175.4 (3)	C30—N8—C25—N7	−2.7 (5)
C11—N2—C15—C14	−3.2 (5)	C30—N8—C25—C24	179.8 (3)

**Chlorido[tris(pyridin-2-yl)amine- $\kappa^2$ N,N']**[tris(pyridin-2-yl)amine- $\kappa^3$ N,N',N'']**ruthenium(II)**  
**hexafluoroantimonate chloroform monosolvate (2b)**

*Crystal data*

[RuCl(C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>)<sub>2</sub>][SbF<sub>6</sub>]·CHCl<sub>3</sub>  
*M<sub>r</sub>* = 988.21  
 Monoclinic, *P*2<sub>1</sub>/*n*  
*a* = 8.3209 (3) Å  
*b* = 27.3213 (10) Å  
*c* = 15.7839 (6) Å  
 $\beta$  = 99.554 (4)°  
*V* = 3538.5 (2) Å<sup>3</sup>  
*Z* = 4

*F*(000) = 1936  
*D<sub>x</sub>* = 1.855 Mg m<sup>−3</sup>  
 Mo *K* $\alpha$  radiation,  $\lambda$  = 0.71073 Å  
 Cell parameters from 8950 reflections  
 $\theta$  = 3.3–30.4°  
 $\mu$  = 1.56 mm<sup>−1</sup>  
*T* = 93 K  
 Needle, yellow  
 0.2 × 0.04 × 0.01 mm

*Data collection*

Dectris Pilatus 3R  
 diffractometer  
 Detector resolution: 5.8 pixels mm<sup>−1</sup>  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (CrysAlis PRO; Rigaku OD, 2019)  
*T<sub>min</sub>* = 0.783, *T<sub>max</sub>* = 1.000  
 32718 measured reflections

8658 independent reflections  
 6339 reflections with *I* > 2 $\sigma$ (*I*)  
*R<sub>int</sub>* = 0.067  
 $\theta_{\max}$  = 28.3°,  $\theta_{\min}$  = 2.7°  
*h* = −10→11  
*k* = −36→36  
*l* = −21→21

*Refinement*

Refinement on *F*<sup>2</sup>  
 Least-squares matrix: full  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.048  
*wR*(*F*<sup>2</sup>) = 0.081  
*S* = 1.08  
 8658 reflections  
 460 parameters  
 0 restraints  
 Primary atom site location: iterative

Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0259P)^2 + 4.6355P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max}$  = 0.001  
 $\Delta\rho_{\max}$  = 0.98 e Å<sup>−3</sup>  
 $\Delta\rho_{\min}$  = −1.31 e Å<sup>−3</sup>

*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 (Å<sup>2</sup>)*

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>iso</sub></i> */ <i>U<sub>eq</sub></i>
Sb1	0.69166 (3)	0.62728 (2)	−0.05383 (2)	0.01521 (7)
F1	0.6827 (4)	0.59602 (10)	0.05068 (15)	0.0327 (7)
F2	0.5627 (3)	0.67836 (9)	−0.02234 (18)	0.0328 (7)
F3	0.8788 (3)	0.66146 (10)	−0.00166 (16)	0.0287 (6)
F4	0.8247 (3)	0.57702 (10)	−0.08400 (18)	0.0355 (7)

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F5	0.5049 (3)	0.59389 (11)	-0.10526 (17)	0.0349 (7)
F6	0.7015 (4)	0.65920 (12)	-0.15811 (16)	0.0418 (8)
Ru1	0.58927 (4)	0.60754 (2)	0.30593 (2)	0.00852 (7)
Cl1	0.77395 (11)	0.59764 (3)	0.44096 (5)	0.01372 (19)
N2	0.7417 (4)	0.56320 (12)	0.24889 (19)	0.0107 (6)
N3	0.4391 (4)	0.60839 (12)	0.18936 (19)	0.0115 (6)
N1	0.4703 (4)	0.54419 (11)	0.32919 (19)	0.0113 (7)
N4	0.4977 (4)	0.52254 (12)	0.18626 (18)	0.0115 (7)
N5	0.7063 (4)	0.67232 (12)	0.28082 (19)	0.0115 (7)
N6	0.4277 (4)	0.65211 (12)	0.35747 (19)	0.0117 (7)
N8	0.6459 (4)	0.70582 (12)	0.40989 (19)	0.0123 (7)
N7	0.8885 (4)	0.72276 (13)	0.5000 (2)	0.0177 (7)
C6	0.9055 (5)	0.56764 (15)	0.2601 (2)	0.0141 (8)
H6	0.957103	0.592094	0.297909	0.017*
C7	0.9997 (5)	0.53763 (15)	0.2181 (3)	0.0185 (9)
H7	1.114568	0.541992	0.226651	0.022*
C8	0.9284 (5)	0.50120 (15)	0.1636 (2)	0.0185 (9)
H8	0.992479	0.480445	0.134202	0.022*
C9	0.7597 (5)	0.49589 (15)	0.1530 (2)	0.0152 (8)
H9	0.706172	0.470935	0.117000	0.018*
C10	0.6719 (5)	0.52755 (14)	0.1958 (2)	0.0118 (8)
C11	0.3591 (5)	0.64812 (15)	0.1527 (2)	0.0162 (8)
H11	0.378994	0.678958	0.180210	0.019*
C12	0.2496 (5)	0.64568 (16)	0.0766 (2)	0.0186 (9)
H12	0.195487	0.674313	0.052487	0.022*
C13	0.2198 (5)	0.60054 (17)	0.0360 (3)	0.0218 (10)
H13	0.143533	0.597921	-0.015685	0.026*
C14	0.3023 (5)	0.55957 (16)	0.0716 (2)	0.0158 (8)
H14	0.284818	0.528513	0.044608	0.019*
C15	0.4114 (5)	0.56490 (15)	0.1478 (2)	0.0127 (8)
C1	0.4138 (5)	0.53416 (15)	0.4028 (2)	0.0146 (8)
H1	0.427994	0.557844	0.447456	0.017*
C2	0.3361 (5)	0.49068 (16)	0.4153 (3)	0.0181 (9)
H2	0.295013	0.485214	0.467210	0.022*
C3	0.3185 (5)	0.45529 (15)	0.3522 (3)	0.0177 (9)
H3	0.269121	0.424770	0.360926	0.021*
C4	0.3740 (5)	0.46486 (15)	0.2756 (2)	0.0171 (9)
H4	0.362905	0.441262	0.230780	0.021*
C5	0.4461 (4)	0.50989 (14)	0.2664 (2)	0.0118 (8)
C16	0.7696 (5)	0.67804 (15)	0.2075 (2)	0.0142 (8)
H16	0.755458	0.652306	0.166493	0.017*
C17	0.8538 (5)	0.71946 (16)	0.1895 (2)	0.0176 (9)
H17	0.898884	0.721472	0.138081	0.021*
C18	0.8713 (5)	0.75793 (16)	0.2476 (3)	0.0188 (9)
H18	0.928272	0.786806	0.236878	0.023*
C19	0.8034 (5)	0.75320 (15)	0.3218 (2)	0.0152 (8)
H19	0.811851	0.779197	0.362252	0.018*
C20	0.7234 (4)	0.71047 (14)	0.3365 (2)	0.0113 (8)

C21	0.2662 (5)	0.64252 (15)	0.3464 (2)	0.0162 (8)
H21	0.228360	0.612872	0.318558	0.019*
C22	0.1540 (5)	0.67308 (16)	0.3730 (3)	0.0192 (9)
H22	0.042697	0.663737	0.366764	0.023*
C23	0.2053 (5)	0.71796 (16)	0.4093 (3)	0.0188 (9)
H23	0.129180	0.740390	0.426053	0.023*
C24	0.3687 (5)	0.72921 (15)	0.4203 (2)	0.0163 (9)
H24	0.407285	0.759756	0.444306	0.020*
C25	0.4759 (5)	0.69520 (14)	0.3959 (2)	0.0120 (8)
C26	0.9761 (5)	0.72691 (16)	0.5791 (3)	0.0207 (9)
H26	1.087385	0.736011	0.583817	0.025*
C27	0.9150 (6)	0.71882 (17)	0.6538 (3)	0.0244 (10)
H27	0.982144	0.721872	0.708417	0.029*
C28	0.7517 (6)	0.70605 (17)	0.6463 (3)	0.0249 (10)
H28	0.705096	0.700071	0.696331	0.030*
C29	0.6573 (5)	0.70206 (16)	0.5659 (2)	0.0200 (9)
H29	0.545079	0.693674	0.559312	0.024*
C30	0.7328 (5)	0.71082 (14)	0.4946 (2)	0.0119 (8)
Cl2	1.1042 (2)	0.60896 (5)	0.71672 (8)	0.0461 (4)
Cl3	1.30678 (17)	0.62246 (5)	0.58615 (9)	0.0424 (3)
Cl4	1.14129 (16)	0.53000 (4)	0.59932 (7)	0.0312 (3)
C31	1.1291 (6)	0.59395 (18)	0.6109 (3)	0.0276 (11)
H31	1.032515	0.606278	0.570191	0.033*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Sb1	0.01827 (14)	0.01482 (14)	0.01267 (12)	−0.00029 (12)	0.00293 (10)	−0.00067 (11)
F1	0.0493 (18)	0.0286 (16)	0.0210 (12)	−0.0020 (13)	0.0081 (12)	0.0090 (11)
F2	0.0367 (16)	0.0175 (14)	0.0473 (16)	0.0085 (12)	0.0158 (13)	−0.0011 (12)
F3	0.0255 (14)	0.0242 (15)	0.0340 (14)	−0.0069 (12)	−0.0024 (11)	−0.0018 (11)
F4	0.0293 (15)	0.0330 (16)	0.0441 (16)	0.0110 (13)	0.0061 (13)	−0.0165 (13)
F5	0.0266 (15)	0.0394 (17)	0.0378 (15)	−0.0092 (13)	0.0028 (12)	−0.0125 (13)
F6	0.0501 (19)	0.057 (2)	0.0188 (13)	−0.0019 (17)	0.0086 (13)	0.0155 (13)
Ru1	0.00651 (14)	0.00916 (15)	0.00999 (13)	−0.00014 (12)	0.00161 (11)	−0.00153 (12)
Cl1	0.0134 (4)	0.0141 (5)	0.0128 (4)	−0.0008 (4)	−0.0006 (3)	0.0000 (3)
N2	0.0101 (16)	0.0118 (16)	0.0107 (14)	−0.0015 (13)	0.0034 (13)	−0.0018 (13)
N3	0.0066 (15)	0.0152 (16)	0.0132 (14)	−0.0016 (13)	0.0030 (12)	0.0003 (13)
N1	0.0103 (16)	0.0102 (17)	0.0133 (15)	0.0011 (13)	0.0017 (13)	−0.0002 (13)
N4	0.0149 (17)	0.0120 (17)	0.0083 (14)	−0.0024 (13)	0.0041 (13)	−0.0024 (12)
N5	0.0076 (15)	0.0140 (17)	0.0129 (15)	0.0003 (13)	0.0014 (12)	0.0003 (13)
N6	0.0064 (15)	0.0145 (17)	0.0143 (15)	−0.0013 (13)	0.0022 (12)	−0.0023 (13)
N8	0.0094 (16)	0.0141 (17)	0.0143 (15)	−0.0029 (13)	0.0044 (13)	−0.0040 (13)
N7	0.0153 (18)	0.0180 (19)	0.0198 (17)	−0.0028 (15)	0.0023 (14)	−0.0025 (15)
C6	0.0103 (19)	0.013 (2)	0.0185 (19)	−0.0008 (16)	0.0010 (16)	−0.0029 (16)
C7	0.010 (2)	0.023 (2)	0.024 (2)	0.0020 (17)	0.0073 (17)	0.0005 (18)
C8	0.018 (2)	0.019 (2)	0.019 (2)	0.0042 (17)	0.0066 (17)	−0.0036 (17)
C9	0.018 (2)	0.014 (2)	0.0144 (18)	0.0000 (16)	0.0035 (16)	−0.0029 (16)



C10	0.014 (2)	0.0108 (19)	0.0108 (17)	0.0016 (15)	0.0032 (15)	0.0027 (15)
C11	0.014 (2)	0.015 (2)	0.0193 (19)	-0.0022 (17)	0.0040 (16)	-0.0049 (17)
C12	0.016 (2)	0.019 (2)	0.0185 (19)	0.0048 (17)	-0.0023 (16)	0.0052 (17)
C13	0.018 (2)	0.032 (3)	0.0136 (18)	0.0021 (19)	-0.0008 (16)	0.0024 (18)
C14	0.016 (2)	0.017 (2)	0.0149 (19)	0.0006 (17)	0.0040 (17)	-0.0042 (16)
C15	0.0108 (19)	0.015 (2)	0.0141 (18)	-0.0010 (16)	0.0055 (15)	0.0000 (15)
C1	0.014 (2)	0.019 (2)	0.0109 (17)	0.0005 (16)	0.0040 (15)	-0.0046 (16)
C2	0.018 (2)	0.022 (2)	0.0164 (19)	-0.0009 (18)	0.0063 (17)	0.0022 (17)
C3	0.021 (2)	0.010 (2)	0.023 (2)	-0.0041 (17)	0.0049 (17)	0.0034 (17)
C4	0.020 (2)	0.015 (2)	0.0172 (19)	-0.0013 (17)	0.0048 (17)	-0.0045 (16)
C5	0.0060 (18)	0.016 (2)	0.0129 (17)	0.0031 (15)	-0.0002 (14)	0.0009 (15)
C16	0.0115 (19)	0.016 (2)	0.0142 (18)	0.0013 (16)	-0.0007 (15)	0.0003 (16)
C17	0.016 (2)	0.023 (2)	0.0141 (18)	-0.0013 (17)	0.0035 (16)	0.0016 (17)
C18	0.019 (2)	0.017 (2)	0.021 (2)	-0.0051 (17)	0.0018 (17)	0.0058 (17)
C19	0.013 (2)	0.015 (2)	0.0168 (19)	0.0014 (16)	-0.0001 (16)	0.0000 (16)
C20	0.0064 (18)	0.013 (2)	0.0144 (17)	0.0042 (15)	0.0025 (15)	0.0004 (15)
C21	0.014 (2)	0.014 (2)	0.0209 (19)	-0.0025 (16)	0.0019 (16)	-0.0063 (16)
C22	0.0068 (19)	0.024 (2)	0.027 (2)	-0.0014 (17)	0.0044 (17)	-0.0047 (18)
C23	0.016 (2)	0.019 (2)	0.022 (2)	0.0045 (17)	0.0062 (17)	-0.0069 (18)
C24	0.015 (2)	0.015 (2)	0.0184 (19)	0.0000 (16)	0.0013 (16)	-0.0079 (16)
C25	0.0099 (18)	0.013 (2)	0.0134 (17)	-0.0002 (15)	0.0024 (15)	-0.0005 (15)
C26	0.015 (2)	0.024 (2)	0.022 (2)	-0.0043 (18)	-0.0009 (17)	-0.0065 (18)
C27	0.027 (3)	0.024 (2)	0.019 (2)	0.005 (2)	-0.0061 (19)	-0.0041 (18)
C28	0.027 (3)	0.033 (3)	0.016 (2)	0.005 (2)	0.0080 (19)	0.0019 (19)
C29	0.016 (2)	0.028 (3)	0.017 (2)	-0.0038 (18)	0.0048 (17)	-0.0018 (18)
C30	0.0141 (19)	0.0086 (19)	0.0128 (17)	0.0006 (15)	0.0013 (15)	-0.0034 (15)
Cl2	0.0788 (11)	0.0278 (7)	0.0356 (6)	0.0110 (7)	0.0209 (7)	0.0019 (6)
Cl3	0.0421 (8)	0.0379 (8)	0.0484 (7)	-0.0087 (6)	0.0115 (6)	0.0051 (6)
Cl4	0.0390 (7)	0.0251 (6)	0.0300 (6)	-0.0012 (5)	0.0076 (5)	-0.0012 (5)
C31	0.024 (2)	0.028 (3)	0.030 (2)	0.002 (2)	0.003 (2)	0.005 (2)

*Geometric parameters (Å, °)*

Sb1—F1	1.870 (2)	C12—C13	1.393 (6)
Sb1—F2	1.877 (3)	C13—H13	0.9500
Sb1—F3	1.884 (2)	C13—C14	1.383 (6)
Sb1—F4	1.874 (3)	C14—H14	0.9500
Sb1—F5	1.867 (3)	C14—C15	1.389 (5)
Sb1—F6	1.876 (3)	C1—H1	0.9500
Ru1—Cl1	2.4269 (9)	C1—C2	1.382 (6)
Ru1—N2	2.065 (3)	C2—H2	0.9500
Ru1—N3	2.046 (3)	C2—C3	1.379 (6)
Ru1—N1	2.057 (3)	C3—H3	0.9500
Ru1—N5	2.090 (3)	C3—C4	1.388 (6)
Ru1—N6	2.077 (3)	C4—H4	0.9500
N2—C6	1.350 (5)	C4—C5	1.387 (6)
N2—C10	1.351 (5)	C16—H16	0.9500
N3—C11	1.352 (5)	C16—C17	1.385 (6)

N3—C15	1.358 (5)	C17—H17	0.9500
N1—C1	1.351 (5)	C17—C18	1.387 (6)
N1—C5	1.354 (5)	C18—H18	0.9500
N4—C10	1.439 (5)	C18—C19	1.388 (6)
N4—C15	1.442 (5)	C19—H19	0.9500
N4—C5	1.444 (5)	C19—C20	1.382 (5)
N5—C16	1.357 (5)	C21—H21	0.9500
N5—C20	1.355 (5)	C21—C22	1.369 (6)
N6—C21	1.352 (5)	C22—H22	0.9500
N6—C25	1.354 (5)	C22—C23	1.390 (6)
N8—C20	1.423 (5)	C23—H23	0.9500
N8—C25	1.425 (5)	C23—C24	1.376 (6)
N8—C30	1.417 (5)	C24—H24	0.9500
N7—C26	1.341 (5)	C24—C25	1.387 (5)
N7—C30	1.325 (5)	C26—H26	0.9500
C6—H6	0.9500	C26—C27	1.377 (6)
C6—C7	1.378 (6)	C27—H27	0.9500
C7—H7	0.9500	C27—C28	1.389 (7)
C7—C8	1.384 (6)	C28—H28	0.9500
C8—H8	0.9500	C28—C29	1.382 (6)
C8—C9	1.393 (6)	C29—H29	0.9500
C9—H9	0.9500	C29—C30	1.398 (5)
C9—C10	1.379 (5)	C12—C31	1.765 (5)
C11—H11	0.9500	C13—C31	1.771 (5)
C11—C12	1.383 (5)	C14—C31	1.761 (5)
C12—H12	0.9500	C31—H31	1.0000
F1—Sb1—F2	89.87 (12)	C14—C13—C12	119.4 (4)
F1—Sb1—F3	89.53 (12)	C14—C13—H13	120.3
F1—Sb1—F4	90.06 (13)	C13—C14—H14	120.8
F1—Sb1—F6	179.44 (13)	C13—C14—C15	118.4 (4)
F2—Sb1—F3	89.04 (12)	C15—C14—H14	120.8
F4—Sb1—F2	178.69 (13)	N3—C15—N4	117.8 (3)
F4—Sb1—F3	89.66 (12)	N3—C15—C14	122.9 (4)
F4—Sb1—F6	90.24 (14)	C14—C15—N4	119.2 (3)
F5—Sb1—F1	90.47 (13)	N1—C1—H1	118.8
F5—Sb1—F2	90.42 (13)	N1—C1—C2	122.4 (4)
F5—Sb1—F3	179.46 (13)	C2—C1—H1	118.8
F5—Sb1—F4	90.88 (13)	C1—C2—H2	120.2
F5—Sb1—F6	90.00 (13)	C3—C2—C1	119.6 (4)
F6—Sb1—F2	89.82 (13)	C3—C2—H2	120.2
F6—Sb1—F3	89.99 (13)	C2—C3—H3	120.4
N2—Ru1—C11	88.41 (9)	C2—C3—C4	119.1 (4)
N2—Ru1—N5	94.29 (12)	C4—C3—H3	120.4
N2—Ru1—N6	177.10 (12)	C3—C4—H4	121.0
N3—Ru1—C11	173.96 (10)	C5—C4—C3	118.0 (4)
N3—Ru1—N2	86.69 (12)	C5—C4—H4	121.0
N3—Ru1—N1	85.98 (12)	N1—C5—N4	116.5 (3)

N3—Ru1—N5	93.11 (12)	N1—C5—C4	123.5 (3)
N3—Ru1—N6	90.41 (12)	C4—C5—N4	120.0 (3)
N1—Ru1—C11	90.16 (9)	N5—C16—H16	118.3
N1—Ru1—N2	86.14 (12)	N5—C16—C17	123.4 (4)
N1—Ru1—N5	178.97 (12)	C17—C16—H16	118.3
N1—Ru1—N6	93.53 (13)	C16—C17—H17	120.5
N5—Ru1—C11	90.79 (8)	C16—C17—C18	119.0 (4)
N6—Ru1—C11	94.47 (8)	C18—C17—H17	120.5
N6—Ru1—N5	85.99 (13)	C17—C18—H18	120.8
C6—N2—Ru1	124.7 (3)	C17—C18—C19	118.4 (4)
C6—N2—C10	117.8 (3)	C19—C18—H18	120.8
C10—N2—Ru1	117.5 (3)	C18—C19—H19	120.2
C11—N3—Ru1	125.3 (3)	C20—C19—C18	119.6 (4)
C11—N3—C15	117.6 (3)	C20—C19—H19	120.2
C15—N3—Ru1	117.0 (3)	N5—C20—N8	116.5 (3)
C1—N1—Ru1	124.8 (3)	N5—C20—C19	122.9 (4)
C1—N1—C5	117.2 (3)	C19—C20—N8	120.5 (3)
C5—N1—Ru1	118.0 (3)	N6—C21—H21	118.1
C10—N4—C15	113.0 (3)	N6—C21—C22	123.8 (4)
C10—N4—C5	111.8 (3)	C22—C21—H21	118.1
C15—N4—C5	111.2 (3)	C21—C22—H22	120.5
C16—N5—Ru1	121.2 (3)	C21—C22—C23	119.1 (4)
C20—N5—Ru1	122.0 (2)	C23—C22—H22	120.5
C20—N5—C16	116.7 (3)	C22—C23—H23	120.7
C21—N6—Ru1	122.0 (3)	C24—C23—C22	118.6 (4)
C21—N6—C25	116.1 (3)	C24—C23—H23	120.7
C25—N6—Ru1	121.5 (3)	C23—C24—H24	120.6
C20—N8—C25	117.7 (3)	C23—C24—C25	118.9 (4)
C30—N8—C20	122.1 (3)	C25—C24—H24	120.6
C30—N8—C25	120.3 (3)	N6—C25—N8	117.3 (3)
C30—N7—C26	117.0 (4)	N6—C25—C24	123.4 (4)
N2—C6—H6	119.1	C24—C25—N8	119.2 (3)
N2—C6—C7	121.8 (4)	N7—C26—H26	117.9
C7—C6—H6	119.1	N7—C26—C27	124.3 (4)
C6—C7—H7	119.8	C27—C26—H26	117.9
C6—C7—C8	120.5 (4)	C26—C27—H27	121.2
C8—C7—H7	119.8	C26—C27—C28	117.5 (4)
C7—C8—H8	121.0	C28—C27—H27	121.2
C7—C8—C9	118.0 (4)	C27—C28—H28	120.1
C9—C8—H8	121.0	C29—C28—C27	119.8 (4)
C8—C9—H9	120.6	C29—C28—H28	120.1
C10—C9—C8	118.8 (4)	C28—C29—H29	121.2
C10—C9—H9	120.6	C28—C29—C30	117.6 (4)
N2—C10—N4	117.1 (3)	C30—C29—H29	121.2
N2—C10—C9	123.2 (4)	N7—C30—N8	115.1 (3)
C9—C10—N4	119.7 (3)	N7—C30—C29	123.8 (3)
N3—C11—H11	118.7	C29—C30—N8	121.0 (3)
N3—C11—C12	122.7 (4)	C12—C31—C13	109.9 (3)

C12—C11—H11	118.7	C12—C31—H31	108.8
C11—C12—H12	120.6	C13—C31—H31	108.8
C11—C12—C13	118.9 (4)	C14—C31—C12	110.3 (3)
C13—C12—H12	120.6	C14—C31—C13	110.4 (3)
C12—C13—H13	120.3	C14—C31—H31	108.8
Ru1—N2—C6—C7	-178.1 (3)	C1—N1—C5—C4	-3.0 (5)
Ru1—N2—C10—N4	-2.2 (4)	C1—C2—C3—C4	-2.4 (6)
Ru1—N2—C10—C9	179.2 (3)	C2—C3—C4—C5	0.4 (6)
Ru1—N3—C11—C12	-175.0 (3)	C3—C4—C5—N1	2.4 (6)
Ru1—N3—C15—N4	-3.9 (4)	C3—C4—C5—N4	-176.7 (3)
Ru1—N3—C15—C14	174.8 (3)	C5—N1—C1—C2	0.8 (6)
Ru1—N1—C1—C2	-179.3 (3)	C5—N4—C10—N2	-62.6 (4)
Ru1—N1—C5—N4	-3.8 (4)	C5—N4—C10—C9	116.0 (4)
Ru1—N1—C5—C4	177.1 (3)	C5—N4—C15—N3	66.4 (4)
Ru1—N5—C16—C17	-177.4 (3)	C5—N4—C15—C14	-112.4 (4)
Ru1—N5—C20—N8	-5.0 (4)	C16—N5—C20—N8	175.2 (3)
Ru1—N5—C20—C19	178.6 (3)	C16—N5—C20—C19	-1.2 (5)
Ru1—N6—C21—C22	-174.3 (3)	C16—C17—C18—C19	0.1 (6)
Ru1—N6—C25—N8	-8.2 (5)	C17—C18—C19—C20	1.1 (6)
Ru1—N6—C25—C24	170.7 (3)	C18—C19—C20—N5	-0.5 (6)
N2—C6—C7—C8	-1.0 (6)	C18—C19—C20—N8	-176.8 (3)
N3—C11—C12—C13	0.1 (6)	C20—N5—C16—C17	2.4 (5)
N1—C1—C2—C3	1.8 (6)	C20—N8—C25—N6	62.8 (5)
N5—C16—C17—C18	-1.9 (6)	C20—N8—C25—C24	-116.1 (4)
N6—C21—C22—C23	3.8 (6)	C20—N8—C30—N7	3.6 (5)
N7—C26—C27—C28	-0.7 (7)	C20—N8—C30—C29	-174.6 (4)
C6—N2—C10—N4	178.5 (3)	C21—N6—C25—N8	178.8 (3)
C6—N2—C10—C9	-0.1 (5)	C21—N6—C25—C24	-2.4 (6)
C6—C7—C8—C9	-0.2 (6)	C21—C22—C23—C24	-2.6 (6)
C7—C8—C9—C10	1.2 (6)	C22—C23—C24—C25	-0.8 (6)
C8—C9—C10—N2	-1.1 (6)	C23—C24—C25—N6	3.4 (6)
C8—C9—C10—N4	-179.6 (3)	C23—C24—C25—N8	-177.8 (4)
C10—N2—C6—C7	1.1 (6)	C25—N6—C21—C22	-1.3 (6)
C10—N4—C15—N3	-60.3 (4)	C25—N8—C20—N5	-54.6 (5)
C10—N4—C15—C14	120.9 (4)	C25—N8—C20—C19	121.9 (4)
C10—N4—C5—N1	66.4 (4)	C25—N8—C30—N7	-177.2 (4)
C10—N4—C5—C4	-114.5 (4)	C25—N8—C30—C29	4.6 (6)
C11—N3—C15—N4	179.4 (3)	C26—N7—C30—N8	-178.7 (4)
C11—N3—C15—C14	-1.9 (6)	C26—N7—C30—C29	-0.6 (6)
C11—C12—C13—C14	-1.2 (6)	C26—C27—C28—C29	-0.2 (7)
C12—C13—C14—C15	0.8 (6)	C27—C28—C29—C30	0.6 (7)
C13—C14—C15—N3	0.8 (6)	C28—C29—C30—N8	177.8 (4)
C13—C14—C15—N4	179.6 (4)	C28—C29—C30—N7	-0.2 (7)
C15—N3—C11—C12	1.4 (6)	C30—N8—C20—N5	124.6 (4)
C15—N4—C10—N2	63.7 (4)	C30—N8—C20—C19	-58.9 (5)
C15—N4—C10—C9	-117.6 (4)	C30—N8—C25—N6	-116.4 (4)
C15—N4—C5—N1	-60.9 (4)	C30—N8—C25—C24	64.7 (5)

C15—N4—C5—C4	118.2 (4)	C30—N7—C26—C27	1.1 (7)
C1—N1—C5—N4	176.1 (3)		

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