

## Bis(di-2-pyridyl sulfide- $\kappa^2N,N'$ )-(4-methylpyrimidin-2-yl 2-pyridylmethyl sulfide- $\kappa^2N,S$ )ruthenium(II) bis(hexafluorophosphate) acetonitrile solvate

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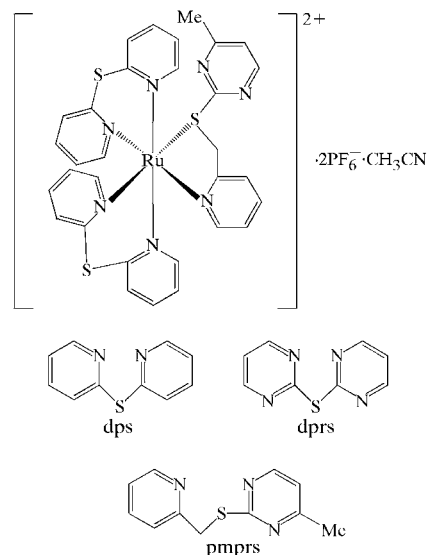
The crystal structure of the title compound,  $[\text{Ru}(\text{C}_{10}\text{H}_8\text{N}_2\text{S})_2(\text{C}_{11}\text{H}_{11}\text{N}_3\text{S})](\text{PF}_6)_2 \cdot \text{C}_2\text{H}_3\text{N}$ , is composed of a bivalent octahedral  $\text{Ru}^{\text{II}}$  complex, two  $\text{PF}_6^-$  anions and an acetonitrile solvent molecule. Two  $\text{PF}_6^-$  units are found on a crystallographic binary axis, therefore contributing just one half each to the asymmetric unit cell. The structure displays a peculiar stereochemistry of the cation. Three bidentate ligands around the Ru centre, together with the coordination of the non-symmetric S atom, mean that these two atoms are chiral. This would lead to four stereoisomers, but only an enantiomeric pair was found in the analyzed sample.

### Comment

The coordination chemistry of flexible and hemilabile ligands, containing both inert and labile groups, is an active area of research (Slone *et al.*, 1999; Vagg, 1987). Heterocyclic N-atom donors are often good ligands for many transition metal centres. Hybrid S/N/S ligands consisting of inert pyridine or bipyridine binding groups, connected to labile sulfur-binding sites, show S–S switching in addition to S inversion (Abel *et al.*, 1995, and references therein). Thioether ligands containing aromatic nitrogen heterocycles, such as di-2-pyridyl sulfide or di-2-pyrimidyl sulfide (dps and dprs), usually bind metals in an  $N,N'$ -bidentate fashion (Bruno *et al.*, 1995, and references therein) and sometimes adopt  $N$ -monodentate coordination (Tresoldi *et al.*, 1991, 1992), or  $N:N'$ - (De Munno *et al.*, 1993; Teles *et al.* 1999) or  $N,N':S$ -bridging coordination (Anderson & Steel, 1998). The flexibility and, in a few cases, the hemilability of dps have been assessed (Tresoldi *et al.*, 1992; De Munno *et al.* 1993).

Recently, we have demonstrated that dps, under appropriate conditions, binds Ru in an  $N,S$ -chelate fashion, leaving one of the pyridine rings uncoordinated (Scopelliti *et al.*,

2001). In such species, some dynamic processes occur, as shown by the temperature dependence of the NMR spectra, but only the restricted rotation of the uncoordinated ring could be studied, whereas the total dynamic stereochemistry remained unclear. On the other hand, we have demonstrated the presence of two invertomers as enantiomeric pairs ( $\Delta R, \Delta S$  and  $\Delta S, \Delta R$ ) and obtained quantitative information on the activation energy of the pyramidal inversion around the coordinated S atom (Tresoldi *et al.*, 2002), as well as of the restricted rotation of the pendant ring (Baradello *et al.*, 2004), when the  $\text{Ru}^{\text{II}}$  centre is  $N,S$ -chelated by thioether ligands based on pyridine or pyrimidine and benzyl or phenyl derivatives. We have now turned our attention to metal complexes containing unsymmetrical NSNN thioethers, and we are interested in studying the interchange processes between different conformations and distinct coordination species. In this paper, the reaction of 4-methylpyrimidin-2-yl 2-pyridylmethyl sulfide (pmprs) with *cis*- $\text{Ru}(\text{dps}-N,N')_2\text{Cl}_2$  led to the title compound,  $[\text{Ru}(\text{dps}-N,N')_2\text{pmprs}](\text{PF}_6)_2 \cdot \text{C}_2\text{H}_3\text{N}$ , (I).



The structure of (I) presents two asymmetric atoms, Ru1 and S34, the conventional absolute configurations of which are  $\Delta$  and  $R$ , respectively. Since the space group is centrosymmetric, a racemic mixture crystallizes in the solid state ( $\Delta R$  and  $\Delta S$  enantiomers; Fig. 1). The asymmetric unit consists of one cationic complex, one acetonitrile solvent molecule, one entire hexafluorophosphate unit, and two further halves of the same anion located on special positions (along the binary axis). The coordination geometry of the  $\text{Ru}^{\text{II}}$  ion is, as expected, distorted octahedral, with five N atoms and atom S34 as binding sites (Table 1 and Fig. 1). The distortion provoked by an  $N,S$ -chelating short-bite ligand has already been shown in similar derivatives (Scopelliti *et al.*, 2001). In (I), this effect is not so dramatic, since the five-membered ring presents less strain than the previously analysed four-membered  $N,S$ -chelating short-bite ligand. This is evident from the geometric comparison of the parameters  $\text{N}—\text{Ru}—\text{S}$  [ $81.8(1)$  versus  $67.8(2)^\circ$ ],  $\text{Ru}—\text{N}$  [ $2.123(3)$  versus  $2.080(5)$  Å] and  $\text{Ru}—\text{S}$  [ $2.358(1)$  versus  $2.424(2)$  Å] in (I)

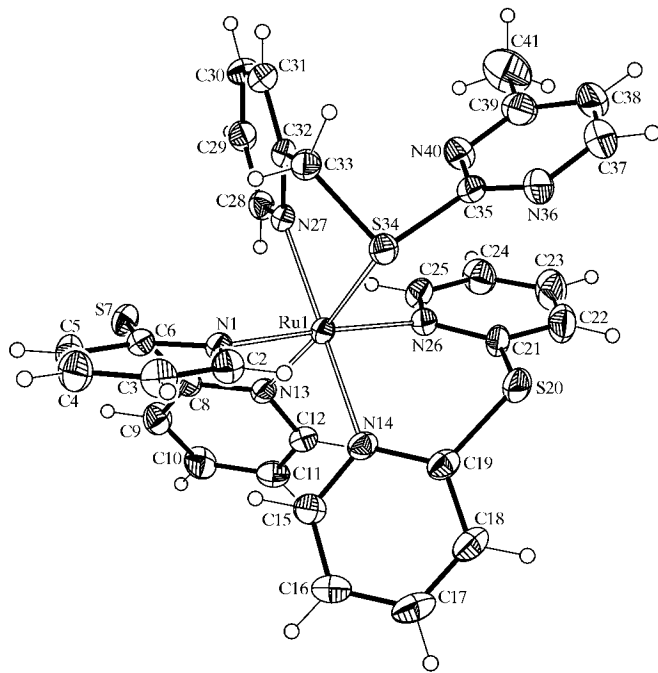
and the above-mentioned structure, respectively. This is confirmed by an analogue of (I) with the pmprs position occupied by a different 2-pyridylmethyl 2-pyridyl sulfide ligand (Baradello *et al.*, 2004). In that case, the geometrical parameters are very close to those measured for (I) [Ru—S = 2.370 (1) Å, Ru—N = 2.108 (3) Å and N—Ru—S = 81.39 (9)°]. The ring formed by the chelation is in an envelope-like conformation, as shown by the puckering parameters (Cremer & Pople, 1975) calculated using the atom sequence from Ru1 to S34 [ $q_2 = 0.489$  (4) Å and  $\varphi_2 = -37.2$  (5)°]. All these data were also compared with Ag (Wang *et al.*, 2001) and Cu (Sillanpää *et al.*, 1994) structures with the symmetric multidentate ligand 2,6-bis(2-pyrimidinylthiomethyl)pyrimidine, which develop (asymmetrically) the same coordination bite shown by pmprs. However, for these structures the other coordination site leads to an enhancement of the distortion. In (I), the Ru—N distances are slightly affected by the pmprs ligand, with the N atoms *trans* to this group being closer to the metal (Table 1). However, none of the Ru—N distances deviate much from the values reported for similar structures (~2.110 Å).

The two dps ligands display their usual 'twisted N,N' inside' conformation, as shown by Bruno *et al.* (1995), in order to chelate the metal *via* the lone pairs of the N atoms. For (I) though, both dps bite angles looks wider with respect to the structure presented by Bruno *et al.* (1995) [N···N = 2.952 (5) and 2.946 (5) Å, and N—Ru—N = 89.0 (1) and 89.1 (1)° for the first and second ligands, respectively]. This is due to the short bite of the pmprs ligand allowing the widening of the dps groups. The boat-like conformation of both dps rings gener-

ated through the above-mentioned chelation is shown by the puckering parameters [for ring Ru1/N1–N13,  $Q = 0.839$  (2) Å,  $\theta = 88.2$  (2) and  $\varphi = 0.7$  (2)°; for ring Ru1/N14–N26,  $Q = 0.904$  (3) Å,  $\theta = 92.4$  (2) and  $\varphi = 175.7$  (3)°].

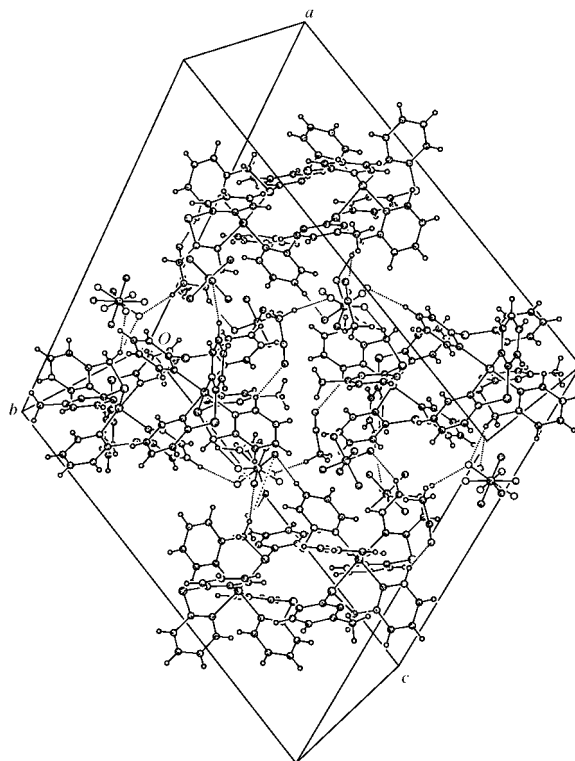
Since there are no structural data available for either the free or the coordinated 4-methylpyrimidin-2-yl 2-pyridylmethyl sulfide (pmprs) ligand, *ab initio* and density functional theory calculations were carried out, using GAUSSIAN98 (Frisch *et al.*, 1998); full geometry optimizations were carried out using the 6-31+G(*d,p*) basis set in order to obtain comparable data and to study how the molecular geometry of pmprs is modified by coordination to a metal centre. As the hybrid B3LYP method generally works better than the Hartree–Fock one in reproducing the 'real' molecular geometry, we compared these calculated values with the experimental X-ray data. As expected, the gas phase conformation of pmprs looks very different from the coordinated one, because of its great conformational flexibility. Nevertheless, we observed a general agreement between the structural parameters, except for the fragment involved in coordination to the metal; the bond distances S34–C35 (1.7728 Å) and S34–C33 (1.8476 Å), and bond angles C33–S34–C35 (103.17°) and N27–C32–C33 (116.14°) can be compared with experimental values for (I) in Table 1.

The crystal packing of (I) is mainly stabilized by intermolecular hydrogen-bond interactions, the acceptor atoms of which are F atoms of the anionic units or the N atom of the solvent molecule, while the donors are several types of C—H groups of the cationic unit. In this way, the complex molecules are mainly held together in an ordered array by the anion and



**Figure 1**

The cation of the  $\Delta$ -Ru1,*R*-S34 isomer of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 35% probability level for all non-C atoms and at the 50% probability level for C atoms. H atoms are shown as small spheres of arbitrary radii.



**Figure 2**

The crystal packing of (I).

the solvent molecule (Table 2). Other weak dipolar intercation interactions further stabilize the overall solid-state structure.

Experimental

Di-2-pyridyl sulfide (dps), 4-methylpyrimidin-2-yl 2-pyridylmethyl sulfide (pmprs) and *cis*-Ru(dps-*N,N'*)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O were prepared according to the methods of Chachaty *et al.* (1976), Haviv *et al.* (1983) and Tresoldi *et al.* (2005), respectively. *cis*-Ru(dps-*N,N'*)<sub>2</sub>Cl<sub>2</sub>·2H<sub>2</sub>O (0.195 g, 0.33 mmol) and pmprs (0.22 g, 3 mmol) were refluxed in ethanol–water (50 ml, 3:2) under N<sub>2</sub> for 3 h. After filtration of the solution into water (80 ml) containing NH<sub>4</sub>PF<sub>6</sub> (0.49 g, 1 mmol), a yellow precipitate was obtained. This was filtered off, washed with water (30 ml) and dried overnight. The solid was then dissolved in acetone (15 ml), precipitated with diethyl ether (70 ml), washed with diethyl ether (30 ml) and dried over P<sub>4</sub>O<sub>10</sub>. Yellow crystals of (I) suitable for X-ray structure investigation were obtained from a solution in acetonitrile–ether (3:1) on standing for *ca* 3 d at 252 K. Analysis, C<sub>32</sub>H<sub>30</sub>F<sub>12</sub>N<sub>8</sub>P<sub>2</sub>RuS<sub>3</sub> requires: C 37.91, H 3.05, N 11.05%; found: C 37.85, H 3.00, N 11.00%.

Crystal data

[Ru(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> S) <sub>2</sub> (C <sub>11</sub> H <sub>11</sub> N <sub>3</sub> S)]· (PF <sub>6</sub> ) <sub>2</sub> ·C <sub>2</sub> H <sub>3</sub> N	<i>D</i> <sub>x</sub> = 1.698 Mg m <sup>-3</sup>
<i>M</i> <sub>r</sub> = 1025.84	Mo <i>K</i> α radiation
Monoclinic, <i>I</i> 2/ <i>a</i>	Cell parameters from 30 reflections
<i>a</i> = 23.685 (5) Å	<i>θ</i> = 2.2–16.2°
<i>b</i> = 14.183 (2) Å	<i>μ</i> = 0.72 mm <sup>-1</sup>
<i>c</i> = 25.264 (8) Å	<i>T</i> = 298 (2) K
<i>β</i> = 108.941 (16)°	Irregular, yellow
<i>V</i> = 8027 (3) Å <sup>3</sup>	0.4 × 0.24 × 0.2 mm
<i>Z</i> = 8	

Data collection

Bruker <i>P4</i> diffractometer	<i>h</i> = −28 → 24
<i>ω</i> scans	<i>k</i> = −16 → 1
8188 measured reflections	<i>l</i> = −30 → 24
7057 independent reflections	3 standard reflections
4940 reflections with <i>I</i> > 2σ( <i>I</i> )	every 197 reflections
<i>R</i> <sub>int</sub> = 0.028	intensity decay: none
<i>θ</i> <sub>max</sub> = 25.0°	

Refinement

Refinement on <i>F</i> <sup>2</sup>	<i>w</i> = 1/[σ <sup>2</sup> ( <i>F</i> <sub>o</sub> <sup>2</sup> ) + (0.0418 <i>P</i> ) <sup>2</sup> + 20.1188 <i>P</i> ]
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )] = 0.050	where <i>P</i> = ( <i>F</i> <sub>o</sub> <sup>2</sup> + 2 <i>F</i> <sub>c</sub> <sup>2</sup> )/3
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.114	(Δσ) <sub>max</sub> = 0.006
<i>S</i> = 1.02	Δρ <sub>max</sub> = 0.59 e Å <sup>-3</sup>
7057 reflections	Δρ <sub>min</sub> = −0.38 e Å <sup>-3</sup>
572 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Ru1–N14	2.095 (4)	C6–S7	1.751 (5)
Ru1–N13	2.102 (4)	S7–C8	1.772 (5)
Ru1–N26	2.106 (4)	C19–S20	1.758 (5)
Ru1–N1	2.109 (4)	S20–C21	1.761 (5)
Ru1–N27	2.123 (4)	C33–S34	1.825 (5)
Ru1–S34	2.3581 (13)	S34–C35	1.816 (5)
N14–Ru1–N13	86.18 (14)	N1–Ru1–N27	92.05 (14)
N14–Ru1–N26	89.08 (15)	N14–Ru1–S34	97.98 (11)
N13–Ru1–N26	91.97 (14)	N13–Ru1–S34	174.46 (10)
N14–Ru1–N1	87.34 (14)	N26–Ru1–S34	91.75 (10)
N13–Ru1–N1	89.05 (14)	N1–Ru1–S34	87.50 (10)
N26–Ru1–N1	176.20 (14)	N27–Ru1–S34	81.82 (10)
N14–Ru1–N27	179.37 (16)	C6–S7–C8	104.6 (2)
N13–Ru1–N27	93.98 (14)	C19–S20–C21	103.9 (2)
N26–Ru1–N27	91.52 (14)	C35–S34–C33	97.2 (2)

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C17–H17···F <sup>i</sup>	0.93	2.50	3.399 (7)	163
C11–H11···F1	0.93	2.51	3.385 (8)	156
C28–H28···N44	0.93	2.58	3.353 (8)	141

Symmetry code: (i) *x*, −*y* + ½, *z* + ½.

X-ray diffraction analysis gave a monoclinic crystal system for (I). The space group was assumed to be centrosymmetric during the data-reduction procedure, and was confirmed by the subsequent analysis (Hahn, 1989). All H atoms were treated as riding, with alkyl C–H distances of 0.98 Å, methyl C–H distances of 0.96 Å and aromatic C–H distances of 0.93 Å. Their isotropic displacement parameters were fixed by the riding-model technique at *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(C) for the methyl H atoms and 1.2*U*<sub>eq</sub>(C) for all others. Intensities were calculated by the profile-fitting procedure (Lehmann & Larsen, 1974). Some refinement trouble was caused by the intrinsic disorder of the two units in the special position. It was necessary to choose two sites for most of the F atoms and their complementary occupancy factors were obtained by refinement and then fixed.

Data collection: *XSCANS* (Siemens, 1989); cell refinement: *XSCANS*; data reduction: *XPREPW* (Bruker, 1997); program(s) used to solve structure: *SIR2002* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XPW* (Bruker, 1997); software used to prepare material for publication: *PARST97* (Nardelli, 1995) and *WinGX-PC* (Version 1.6.4.05; Farrugia, 1999).

The X-ray diffraction data were collected at the Centro Interdipartimentale per la Diffraattometria dei Raggi-X in Messina.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1808). Services for accessing these data are described at the back of the journal.

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