The θ-scan widths used were $(1.00 + 0.3\tan\theta)°$ for (1) and $(0.90 + 0.3\tan\theta)°$ for (2), both at a speed of $4.0°$ min^{-1} (in ω). The weak reflections were rescanned a maximum of four times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak to background counting time. H atoms were located from difference maps and fixed in ideal positions with $U_{iso} = 1.2U_{eq}(C)$. All non-H atoms were refined anisotropically in both cases, with the exception that in (1) the ill-behaved trifluoromethanesulfonate counterion was refined as a rigid group with individual isotropic displacement parameter values. The largest peaks in the final difference map for compound (1) lie very close to the heaviest atoms. The structures were solved by Patterson methods and expanded using Fourier techniques (*PATTY* in *DIRDIF*; Beurskens *et al.*, 1992). All calculations were performed using *TEXSAN* (Molecular Structure Corporation, 1993). *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989) was used for data collection and cell refinement.

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Tris(4,4'-bipyrimidine)ruthenium(II) Bis(hexafluorophosphate) Acetone Solvate

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Abstract

The molecular structure of tris(4,4'-bipyrimidine)-ruthenium(II) $\{[Ru(bpm)_3]^{2+}\}$ in the title compound $\{[Ru(C_8H_6N_4)_3](PF_6)_2.C_3H_6O\}$ is similar to that of tris(2,2'-bipyridine)ruthenium(II) $\{[Ru(bpy)_3]^{2+}\}$. However, replacement of C by N in the heterocyclic ring alters the molecular electrostatic potential of the complex cation and hence the chiral recognition and self-assembling, yielding a crystal-packing pattern that is unique among known structures of related trisdiimine–metal complexes.

Comment

In the course of our work on chiral recognition among trisdiimine–metal complexes (Breu & Catlow, 1995), the crystal structure of the title compound, (I), was determined in order to explore the influence of the molecular electrostatic potential (MEP) on chiral recognition and self-assembling in the crystalline state. Moreover, the lowest electronically excited states of these metal complexes have been studied intensively (*e.g.* Yersin, Huber & Wiedenhofer, 1994).

(I)
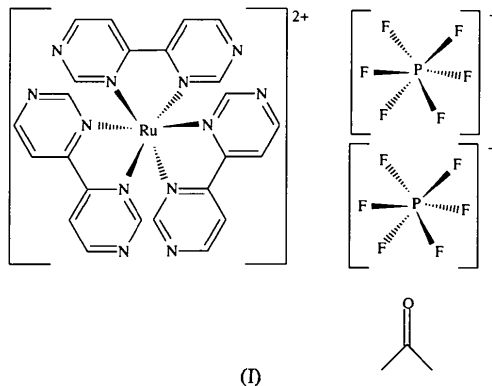
A comparison of the crystal structures of the hexafluorophosphate salts of $[Ru(bpy)_3]^{2+}$, $[Ru(bpym)_3]^{2+}$ and $[Ru(bpz)_3]^{2+}$ (bpym = 2,2'-bipyrimidine, bpz = 2,2'-

bipyrazine) shows that replacement of C by N in the aromatic ring causes little variation in the molecular structures of the complex cations (Rillema, Jones, Woods & Levy, 1992). However, the variation in the MEP due to the introduction and shift of the second N atom induces completely different crystal packing, especially with respect to chiral recognition in the crystal (Breu & Range, 1994). For instance, while $[Ru(bpy)_3]^{2+}$ comprises homochiral layers, $[Ru(bpym)_3]^{2+}$ consists of rigorously racemic layers.

The molecular structure of $[Ru(bpm)_3]^{2+}$ is also very similar to those of $[Ru(bpy)_3]^{2+}$, $[Ru(bpym)_3]^{2+}$ and $[Ru(bpz)_3]^{2+}$. The pyrimidine rings are planar; the maximum deviation from the best plane is 0.013 (4) Å. The dihedral angles between the two planes of each ligand are 7.82 (21) and 8.02 (8)°. Both the complex cation and the acetone crystal solvent possess crystallographically rigorous C_2 symmetry.
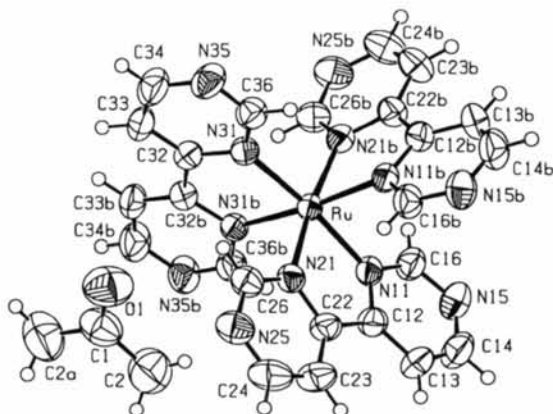

Fig. 1. Molecular structure showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels; H atoms are drawn as small circles of arbitrary radii. Anions are omitted for clarity.

The most interesting feature of the crystal structure is the packing of the complex cations with respect to their chirality. As for many structures of trisdiimine complexes of this kind (Breu & Range, 1994), $[Ru(bpm)_3](PF_6)_2$ comprises layers of complex cations with the counterions sandwiched in between (Fig. 2). The layers consist of zigzag chains of complex cations of the same chirality running along the a axis (Fig. 3). In this respect the packing is similar to that of $[Rh(bpy)_3]Cl_3$ (Hubesch, Mahieu & Meunier-Piret, 1985).

The Ru$\cdots$Ru distance in the homochiral chain is 9.60 Å, while the distance to the Ru in the adjacent chain of alternate configuration is 10.10 Å. Between the almost parallel bipyrimidine ligands of adjacent complexes in the chain, the acetone solvent, with the carbonyl head first, protrudes alternately from above and below into the layer. However, whereas in $[Rh(bpy)_3]Cl_3$ the complex cations are arranged with
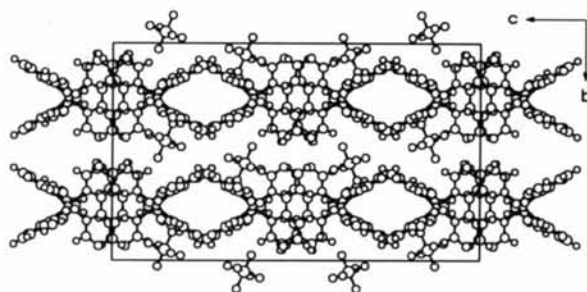

Fig. 2. Packing diagram viewed down the a axis. Note the layers comprised of complex cations and acetone solvent separated by anion layers.
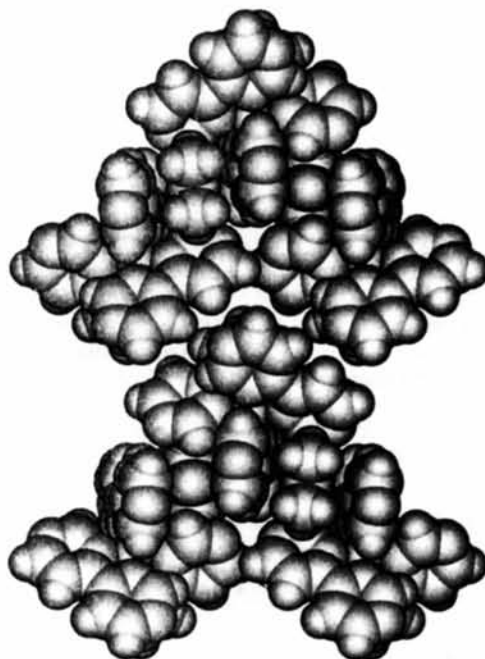

Fig. 3. Space-filling packing diagram of the complex cation layers viewed down the b axis.

their C_3 axes parallel and perpendicular to the layers, in $[Ru(bpm)_3](PF_6)_2$ the C_3 axes of adjacent complex molecules in the homochiral chain are perpendicular to each other and tilted with respect to the layer. Because of the different MEP, the molecular and chiral recognition among the complex cations is modified, yielding a crystal-packing pattern that is unique among known structures of related trisdiimine–metal complexes.

Experimental

The title compound was synthesized by refluxing $RuCl_3.3H_2O$ with a stoichiometric amount of 4,4′-bipyrimidine in water as solvent for 6 min in a microwave oven. Purification was performed by chromatographic methods (De Cola et al., 1993). Suitable single crystals were obtained from an aqueous acetone solution by slow evaporation.

Crystal data

[Ru(C$_8$H$_6$N$_4$)$_3$](PF$_6$)$_2$.C$_3$H$_6$O
$M_r = 923.59$
Orthorhombic
Ibca
$a = 12.007\,(3)$ Å
$b = 18.708\,(5)$ Å
$c = 31.213\,(10)$ Å
$V = 7011\,(3)$ Å^3
$Z = 8$
$D_x = 1.750$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 242
  reflections
$\theta = 3.55$–$24.09°$
$\mu = 0.65$ mm^{-1}
$T = 293\,(2)$ K
Lath
$0.35 \times 0.25 \times 0.10$ mm
Red

Data collection

Stoe IPDS diffractometer
Rotation scans
Absorption correction:
  none
12 605 measured reflections
2763 independent reflections

2160 observed reflections
  $[I > 2\sigma(I)]$
$R_{int} = 0.0419$
$\theta_{max} = 24.09°$
$h = -11 \rightarrow 13$
$k = -21 \rightarrow 18$
$l = -35 \rightarrow 35$

Refinement

Refinement on F^2
$R(F) = 0.0387$
$wR(F^2) = 0.1109$
$S = 1.056$
2763 reflections
252 parameters
All H-atom parameters
  refined
$w = 1/[\sigma^2(F_o^2) + (0.0915P)^2 + 1.6232P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.468$ e Å^{-3}
$\Delta\rho_{min} = -0.524$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables*
  for Crystallography (1992,
  Vol. C, Tables 4.2.6.8 and
  6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Ru	1/2	1/4	0.11992 (1)	0.0366 (2)
N11	0.4978 (2)	0.1764 (2)	0.16976 (9)	0.0444 (11)
N15	0.5803 (3)	0.1188 (2)	0.22997 (10)	0.0673 (14)
N21	0.3315 (3)	0.2264 (2)	0.12421 (8)	0.0440 (10)
N25	0.1425 (3)	0.2336 (2)	0.10117 (13)	0.0657 (14)
N31	0.4843 (2)	0.31921 (15)	0.06820 (9)	0.0417 (12)
N35	0.4477 (3)	0.4320 (2)	0.03628 (10)	0.0653 (14)
C12	0.3944 (3)	0.1567 (2)	0.18373 (11)	0.0493 (12)
C13	0.3821 (4)	0.1184 (2)	0.22101 (12)	0.0643 (14)
C14	0.4773 (4)	0.1006 (3)	0.24290 (14)	0.0737 (18)
C16	0.5854 (3)	0.1551 (2)	0.19368 (11)	0.0550 (12)
C22	0.3011 (3)	0.1819 (2)	0.15631 (11)	0.0497 (12)
C23	0.1923 (3)	0.1618 (2)	0.16165 (14)	0.0663 (16)
C24	0.1147 (4)	0.1895 (2)	0.1332 (2)	0.0777 (19)
C26	0.2489 (3)	0.2502 (2)	0.09821 (13)	0.0530 (12)
C32	0.4877 (3)	0.2887 (2)	0.02874 (11)	0.0447 (12)
C33	0.4679 (4)	0.3287 (2)	−0.00767 (11)	0.0577 (14)
C34	0.4480 (4)	0.4009 (2)	−0.00236 (13)	0.0693 (14)
C36	0.4649 (3)	0.3901 (2)	0.06971 (11)	0.0510 (12)
O1	1/4	0.1871 (2)	0	0.105 (2)
C1	1/4	0.1218 (4)	0	0.083 (3)
C2	0.2397 (6)	0.0791 (3)	0.0407 (2)	0.114 (3)
P	0.15372 (10)	0.44854 (6)	0.14201 (4)	0.0667 (4)
F1	0.1461 (3)	0.37040 (13)	0.16247 (9)	0.0913 (12)
F2	0.2027 (3)	0.4752 (2)	0.18626 (10)	0.1163 (14)
F3	0.0335 (3)	0.4650 (2)	0.16006 (11)	0.1157 (14)
F4	0.1012 (4)	0.4204 (2)	0.09958 (9)	0.151 (2)
F5	0.2729 (4)	0.4309 (2)	0.12609 (14)	0.157 (2)
F6	0.1589 (4)	0.5269 (2)	0.12312 (11)	0.1200 (18)

Table 2. *Selected geometric parameters (Å, °)*

Ru—N11	2.078 (3)	N21—C26	1.357 (5)
Ru—N21	2.075 (4)	N25—C24	1.339 (7)
Ru—N31	2.078 (3)	N25—C26	1.318 (5)
N11—C12	1.367 (4)	N31—C32	1.358 (4)
N11—C16	1.350 (4)	N31—C36	1.347 (5)
N15—C14	1.345 (6)	N35—C34	1.339 (5)
N15—C16	1.322 (5)	N35—C36	1.321 (5)
N21—C22	1.353 (5)		
N11—Ru—N21	78.36 (11)	Ru—N21—C26	127.2 (3)
N11—Ru—N31	173.45 (10)	C22—N21—C26	116.6 (3)
N11—Ru—N11^i	83.03 (13)	C24—N25—C26	116.1 (4)
N11—Ru—N21^i	96.03 (11)	Ru—N31—C32	116.1 (2)
N11—Ru—N31^i	99.78 (12)	Ru—N31—C36	127.0 (2)
N21—Ru—N31	95.41 (11)	C32—N31—C36	116.8 (3)
N11^i—Ru—N21	96.03 (11)	C34—N35—C36	116.9 (4)
N21—Ru—N21^i	172.60 (10)	N11—C12—C13	120.6 (4)
N21—Ru—N31^i	90.34 (11)	N11—C12—C22	114.5 (3)
N11^i—Ru—N31	99.78 (12)	N15—C14—C13	123.7 (4)
N21^i—Ru—N31	90.34 (11)	N11—C16—N15	126.1 (3)
N31—Ru—N31^i	78.05 (11)	N21—C22—C12	114.7 (3)
N11^i—Ru—N21^i	78.36 (11)	N21—C22—C23	121.1 (3)
N11^i—Ru—N31^i	173.45 (10)	N25—C24—C23	122.7 (4)
N21^i—Ru—N31^i	95.41 (11)	N21—C26—N25	126.1 (4)
Ru—N11—C12	115.4 (2)	N31—C32—C33	120.9 (3)
Ru—N11—C16	126.9 (2)	N31—C32—C32^i	114.7 (3)
C12—N11—C16	116.9 (3)	N35—C34—C33	122.2 (4)
C14—N15—C16	115.5 (4)	N31—C36—N35	125.7 (3)
Ru—N21—C22	116.2 (2)		

Symmetry code: (i) $1 - x$, $\frac{1}{2} - y$, z.

Aromatic H atoms were placed in calculated idealized positions and refined using a riding model with a common isotropic displacement parameter. Methyl H atoms were placed in calculated idealized positions based on difference electron-density synthesis and were allowed to refine with a common isotropic displacement parameter.

Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1993). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *PLATON* (Spek, 1992); *PLUTON* (Spek, 1990); *INSIGHT*II (Biosym Technologies, 1993). Software used to prepare material for publication: *PLATON*.

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fac-Tricarbonyldichloro(tetrahydrofuran)-ruthenium(II)

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Abstract

In the *fac*-[RuCl$_2$(CO)$_3$(thf)] complex, the Ru^{II} has slightly distorted octahedral coordination geometry with the carbonyl ligands in a facial arrangement and the thf *trans* to one of the carbonyls. The dihedral angle between the least-squares plane of the thf and the least-squares plane through the four ligands *cis* to the thf is 90.56 (23)°. The torsion angles about the Ru^{II}—O(thf) bond indicate that the thf ring nearly bisects the angles between *cis* Cl and carbonyl ligands.

Comment

The complex, *fac*-[RuCl$_2$(CO)$_3$(thf)], (I), first reported in 1989 (Reddy, Whitten, Redmill, Varshney & Gray, 1989), is a useful starting material for the synthesis of *cis,cis,trans*-[RuCl$_2$(CO)$_2$(phosphine)$_2$] complexes. This is particularly true for *cis,cis,trans*-[RuCl$_2$(CO)$_2$\{Ph$_2$P(CH$_2$CH$_2$O)$_n$CH$_2$CH$_2$PPh$_2$-P,P'\}] metallacrown ethers because the preparation of these complexes requires the simultaneous addition of dilute solutions of [RuCl$_2$(CO)$_3$(thf)] and the ligand (Gray, Varshney & Duffey, 1995). Other Ru^{II} precursors are unsuitable for this reaction because they are generally polymeric and insoluble.

CO
CO_ | _CO
Ru
Cl'''' | '''Cl
O

(I)
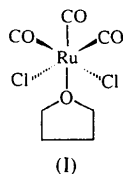
The *fac*-[RuCl$_2$(CO)$_3$(thf)] complex was initially reported as [RuCl$_2$(CO)$_3$].0.75thf based on elemental analysis (Reddy, Whitten, Redmill, Varshney & Gray, 1989). The fractional stoichiometry seemed unlikely, and one reason for obtaining a crystal structure of the complex was to determine the amount of thf present. Other points of interest in the crystal structure are the coordination geometry at the Ru^{II} center and the conformation of the thf ring.

An *ORTEP*II (Johnson, 1976) drawing of *fac*-[RuCl$_2$(CO)$_3$(thf)] is shown in Fig. 1. The coordination geometry of Ru is slightly distorted octahedral, as indicated by the dihedral angles between the three least-squares planes through the Ru and the atoms coordinated to it (90.7, 89.4 and 92.2°). The carbonyl ligands are in a facial arrangement and the thf is *trans* to one of the carbonyls. The thf ring (O4, C4, C5, C6, C7) has an envelope conformation with O4, C4, C5 and C7 forming the base and C5, C6 and C7 forming the flap. The displacement ellipsoid of C7 of thf is elongated relative to this plane, suggesting that, as expected, the ring is conformationally flexible. The dihedral angles between the least-squares plane of the thf (O4, C4, C5, C6, C7) and the least-squares planes containing the Ru, the thf O atom, one of the *cis* carbonyl C atoms, one of the *cis* Cl ligands and the *trans* carbonyl C atom (Ru, Cl1, O4, C1, C3 35.0°; Ru, Cl2, O4, C2, C3 127.2°) indicate that the thf experiences repulsive interactions with the ligands *cis* to it. This potential strain is relieved by a rotation of the thf around the Ru—O4 bond to move C4 into the space between Cl2 and C1, and C7 into the space between Cl1 and C2. The dihedral angle between the least-squares plane of thf (O4, C4, C5, C6, C7) and that formed by the Ru, the two Cl ligands and the two *cis* carbonyl C atoms (Ru, Cl1, Cl2, C1, C2) is 90.56°. This unusual arrangement is consistent with literature reports of other thf complexes (Sobota, Pluzinski, Utko & Lis, 1988; Sobota, Utko & Szafert, 1994).
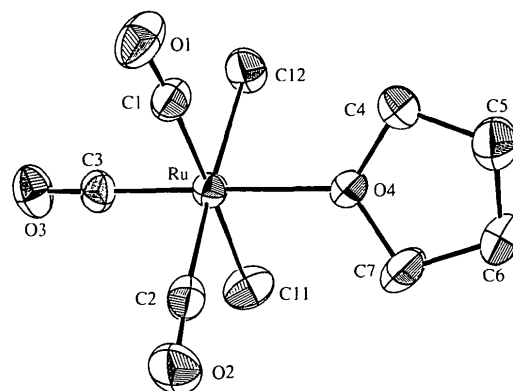

Fig. 1. Drawing of the molecular structure of *fac*-[RuCl$_2$(CO)$_3$(thf)]. Displacement ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.