(Acetonitrile){2,6-bis[1-(2,4,6-tri-methylphenylimino)ethyl]pyridine}-dichloridoruthenium(II) dichloro-methane solvate

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In the title compound, $[RuCl_2(C_2H_3N)(C_{27}H_{31}N_3)]\cdot CH_2Cl_2$, the Ru^{II} ion is six-coordinated in a distorted octahedral arrangement, with the two Cl atoms located in the apical positions, and the pyridine (py) N atom, the two imino N atoms and the acetonitrile N atom located in the basal plane. The two equatorial $Ru-N_{imino}$ distances are almost equal (mean 2.087 Å) and are substantially longer than the equatorial $Ru-N_{py}$ bond [1.921 (4) Å]. It is observed that the $N_{imino}-M-N_{py}$ angle for the five-membered chelate rings of pyridine-2,6-diimine complexes is inversely related to the magnitude of the $M-N_{py}$ bond. The title structure is stabilized by intra- and intermolecular $C-H\cdots Cl$ hydrogen bonds, as well as by van der Waals interactions.

Comment

Pydim [2,6-bis(imino)pyridine] complexes of the form of (I) (see scheme), with a variety of aryl (Ar) substituents, display a range of catalytic activities. For example, iron and cobalt complexes have been used in alkene polymerization reactions (Small *et al.*, 1998; Tellmann *et al.*, 2005; Bryliakov *et al.*, 2004; Ionkin *et al.*, 2006). Ruthenium complexes have been studied for potential applications such as optical sensors and chemical catalysis (Bianchini & Lee, 2000; Ertekin *et al.*, 2003; Çetinkaya *et al.*, 1999; Dayan & Çetinkaya, 2007). More recently, Ru^{II} complexes have been used for transfer hydrogenation reactions of ketones (Dayan & Çetinkaya, 2007).

While Ru^{II}–pydim complexes have been examined extensively, reports of the structural properties of these compounds are rare in the literature (Ertekin *et al.*, 2003; Çetinkaya *et al.*, 1999; Dayan & Çetinkaya, 2007; Özdemir *et al.*, 2007a,b). In order to establish the coordination geometry about the metal atom and to examine the structural parameters in this case, we present here the synthesis and crystal structure of the title complex, (II).
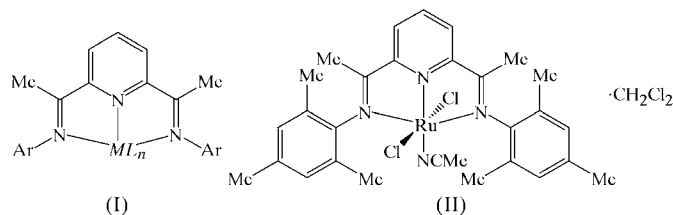
The molecular structure of complex (II) and the atom-labelling scheme are shown in Fig. 1. Selected geometric parameters are listed in Table 1. The mononuclear pydim molecule contains an $(N,N'E,N,N'E)$-N,N'-[1,1'-(pyridine-2,6-diyl)bis(ethan-1-yl-1-ylidene)]bis(2,4,6-trimethylaniline) ligand with an Ru^{II} metal centre, one acetonitrile ligand and two chloride ligands. The compound crystallizes with a dichloromethane solvent molecule in the asymmetric unit and the ligand, with its two imine groups in *ortho* positions with respect to the pyridine (py) N atom, behaves as a symmetrical N,N',N''-tridentate chelate. The five-membered chelate rings formed by atoms Ru1/N1/C1/C17/N3 and Ru1/N1/C5/C6/N2 are planar and the maximum deviations from their planes are 0.072 (3) and 0.041 (3) Å, respectively, for atom N1. These two chelate rings are nearly coplanar, subtending a small dihedral angle of 2.41 (6)°.

The local structure around the Ru^{II} ion of (II) is that of an octahedron, of which the equatorial plane (N1/N2/N3/N4) is formed by three pydim N atoms (N1, N2 and N3) and one acetonitrile N atom (N4). The axial positions in the octahedron are occupied by two Cl atoms (Cl1 and Cl2). As can be seen from the *trans* angles, which vary from 156.97 (16) to 173.90 (5)°, and the *cis* angles, which vary from 78.29 (18) to 108.59 (17)°, the coordination octahedron around the Ru^{II} ion is rather deformed, the major distortion arising *via* the N2—Ru1—N3 angle of 156.97 (16)°. This angle is considerably smaller than the ideal angle of 180° and there is no steric barrier to coordination of a fourth ligand in the equatorial plane *trans* to the pyridine moiety. The N1—Ru—N4 angle, involving the acetonitrile and the pyridine N atoms, is normal at 170.7 (2)°. The Ru—N2 and Ru—N3 bond lengths are comparable with the reported values for $[RuCl_2(pybox-dihydro)(C_2H_4)]$ [pybox is bis(hydrooxazolyl)pyridine; Nishiyama *et al.*, 1995]. However, the $M-N_{py}$ bond [1.921 (4) Å] is somewhat shorter than the $M-N_{imino}$ and $M-N_{MeCN}$ bonds, with the formal double-bond character of the imino linkages N2=C6 and N3=C17 having been retained [C=N = 1.322 (7) and 1.309 (6) Å, respectively]. This coordination environment is similar to that observed in $[RuCl_2(pydim)(CH_3CN)]$ (with Ar = 4-MeOC_6H_4; Çetinkaya *et al.*, 1999).

Complex (II) possesses approximate noncrystallographic C_s symmetry about a plane bisecting the central pyridine ring and containing the metal atom, the acetonitrile N atom and the two halogen atoms. The planes of the benzene rings substituted on the bis(imino)pyridine ligand backbone are, as usual for bis(imino)pyridine ligands, inclined almost orthogonally to

the plane of the backbone [83.2 (2) and 72.5 (2)° for rings C8–C13 and C19–C24, respectively], while the dihedral angle between the two benzene planes is 89.2 (2)°. The geometries at both imino N-atom centres are trigonal planar, the sums of the three bond angles around these centres being 359.4 and 359.9°, and neither is more than *ca* 0.05 Å out of its associated RuC_2 plane.

There are several structures reported in the literature containing various transition metal complexes of pydim-based ligands (Britovsek *et al.*, 1999; Dias *et al.*, 2000; Nakayama *et al.*, 2005; Humphries *et al.*, 2005). Inspection of the the *M*—N bond distances in (II) and in these examples indicates that the two M—N_{imino} bonds are *ca* 0.1–0.2 Å longer than the corresponding M—N_{py} bond within each metal–tridentate chelate unit. Furthermore, it is observed that the N_{imino}—M—N_{py} bond angle for the five-membered chelate rings of pydim complexes is inversely related to the magnitude of the M—N_{py} bond. As the M—N_{py} distance increases from 1.833 (3) Å for [CoMe(pydim)] (with Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$; Humphries *et al.*, 2005) to 1.911 (3) Å for [RhMe(pydim)](OTf)$_2$ (with Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ and where OTf is trifluoromethanesulfonate; Dias *et al.*, 2000) to 1.921 (4) for (II) to 2.001 (3) Å for [CrCl$_3$(pydim)] (with Ar = C$_6$F$_5$; Nakayama *et al.*, 2005) to 2.110 (6) Å for [FeCl$_2$(pydim)] (with Ar = 2,4,6-Me$_3$C$_6$H$_2$; Britovsek *et al.*, 1999), the corresponding average inner 'bite' angle decreases continually from 81.17 to 79.8 to 78.82 to 76.6 to 72.8°, respectively.

The Ru—N_{MeCN} distance is 2.072 (4) Å and this is noticeably longer than the Ru—N_{MeCN} distances in [Ru(C$_5$H$_8$)-(C$_{10}$H$_{15}$)(C$_2$H$_3$N)](CF$_3$SO$_3$) [2.059 (3) Å; Gemel *et al.*, 1999], [Ru(C$_5$H$_5$)(C$_2$H$_3$N)(C$_{18}$H$_{15}$P)$_2$]BF$_4$ [2.040 (3) Å; Carreón *et al.*, 1997] and [RuCl$_2$(C$_2$H$_3$N)$_4$] [2.021 (3) and 2.020 (3) Å; Bown & Hockless, 1996]. This enlargement can be attributed to the different coodination enviroments of the metal atoms. As expected, the acetonitrile ligand is in an almost perfectly linear orientation [N4—C28—C29 = 175.7 (7)°], but with a bent coordination to the Ru^{II} ion [Ru1—N4—C28 = 164.0 (5)°].
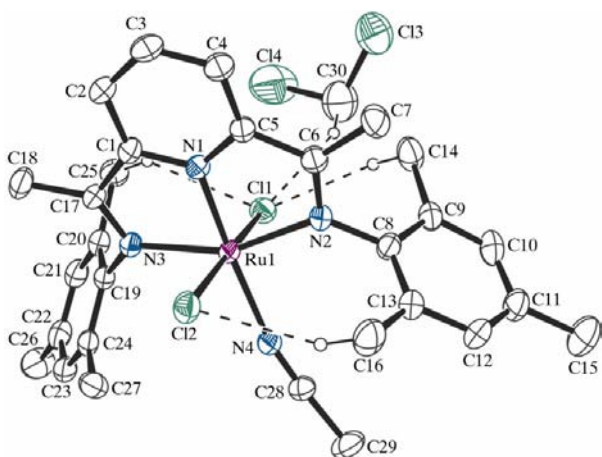

Figure 1
The molecular structure of (II), showing 30% probability displacement ellipsoids and the atom-numbering scheme. Hydrogen bonds are shown as dashed lines. For clarity, only H atoms involved in hydrogen bonding have been included.

Such coordination has been observed in [RuCl$_2$(pydim)-(CH$_3$CN)] [with Ar = 4-MeOC$_6$H$_4$; 173.3 (9)°; Çetinkaya *et al.*, 1999]. A bent metal–acetonitrile coordination is indeed quite common, with angles from 145.2 to 176.9° (average of 167°) having been reported (Agterberg *et al.*, 1998; Begley *et al.*, 1985; Chisholm *et al.*, 1996; Holligan *et al.*, 1992; Libby *et al.*, 1993). This average is somewhat lowered by the two extremely low values for Ni^{II} (145.2°; Holligan *et al.*, 1992) and Mn^{III} (149.1°; Libby *et al.*, 1993) complexes, which have been attributed to hydrogen bonding and steric effects, respectively.

In the molecular structure of (II), three intramolecular interactions are observed between the methyl H atom substituted on the benzene rings and the Cl atoms coordinated to the metal atom (Table 2), which lead to the formation of seven-membered rings with graph-set descriptor *S*(7) (Bernstein *et al.*, 1995). Examination of the structure with *PLATON* (Spek, 2003) reveals that there is an intermolecular interaction between atom Cl1 coordinated to the metal atom and atom H30*B* of the dichloromethane solvent molecule. This interaction is probably responsible for stabilizing the dichloromethane solvent molecule in the observed position. These interactions, together with van der Waals interactions, stabilize the molecular structure and packing. The full geometry of the intra- and intermolecular interactions is given in Table 2.

Experimental

The title complex was synthesized according to the procedure of Dayan & Çetinkaya (2007) and X-ray quality crystals were grown from a solution in CH$_2$Cl$_2$–Et$_2$O (30 ml, 1:3 *v*/*v*).

Crystal data

[RuCl$_2$(C$_2$H$_3$N)(C$_{27}$H$_{31}$N$_3$)]·CH$_2$Cl$_2$	$V = 3218.4$ (3) Å^3
$M_r = 695.50$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 14.4002$ (7) Å	$\mu = 0.85$ mm^{-1}
$b = 14.5478$ (7) Å	$T = 296$ K
$c = 21.0119$ (10) Å	$0.64 \times 0.43 \times 0.12$ mm
$\beta = 133.017$ (3)°	

Data collection

Stoe IPDS2 diffractometer	48037 measured reflections
Absorption correction: integration	7572 independent reflections
(*X-RED32*; Stoe & Cie, 2002)	4762 reflections with $I > 2\sigma(I)$
$T_{min} = 0.526$, $T_{max} = 0.861$	$R_{int} = 0.090$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$	361 parameters
$wR(F^2) = 0.180$	H-atom parameters constrained
$S = 1.08$	$\Delta\rho_{max} = 1.00$ e Å^{-3}
7572 reflections	$\Delta\rho_{min} = -1.08$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Ru1—N1	1.921 (4)	Ru1—N3	2.102 (4)
Ru1—N2	2.072 (4)	Ru1—Cl2	2.3896 (16)
Ru1—N4	2.072 (4)	Ru1—Cl1	2.3982 (16)

H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.96, 0.97 and 0.93 Å for CH$_3$, CH$_2$ and aromatic CH groups, respectively. The displacement parameters of the H atoms were constrained to U_{iso}(H) = 1.2U_{eq}(C), or 1.5U_{eq}(C)

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

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C14—H14$C\cdots$Cl1	0.96	2.51	3.382 (7)	152
C16—H16$C\cdots$Cl2	0.96	2.58	3.442 (8)	150
C25—H25$B\cdots$Cl1	0.96	2.68	3.421 (7)	134
C30—H30$B\cdots$Cl1	0.97	2.75	3.657 (12)	156

for methyl H atoms. Riding methyl H atoms were allowed to rotate freely during refinement using the AFIX 137 command of *SHELXL97* (Sheldrick, 1997). Examination of the refined structure using *PLATON* (Spek, 2003) revealed the presence of void spaces having a total volume of 110.1 Å^3 (3.4%) per unit cell, the volume of the individual voids being 28 Å^3. The maximum peak in the final difference Fourier map is 0.91 Å from atom Ru1 and the minimum peak is 0.88 Å from atom Cl4.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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