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Solvato-polymorph of $[(\eta^6\text{-}C_6H_6)RuCl\ (L)]PF_6$ (L = (2,6-dimethyl-phenyl-pyridin-2-yl methylene amine)

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ABSTRACT

A half-sandwich complex salt of ruthenium containing the Schiff base ligand, 2, 6-dimethyl-*N*-(pyridin-2-ylmethylene)aniline has been synthesized and structurally characterized. The complex salt **1**, $[(\eta^6\text{-}C_6H_6)RuCl(C_5H_4NCH{=}N(2,6\text{-}(CH_3)_2C_6H_3)]PF_6$ was obtained from the reaction of the ruthenium arene precursor, $[(\eta^6\text{-}\ C_6H_6)Ru(\mu\text{-}Cl)Cl]_2$ with the Schiff base in a 1:2 ratio followed by treatment with NH_4PF_6. Its acetone solvate **2**, $[(\eta^6\text{-}C_6H_6)RuCl(C_5H_4NCH{=}N\ (2,\ 6\text{-}\ (CH_3)_2C_6H_3)]PF_6$. $(CH_3)_2CO$ was obtained by recrystallization of **1** from a solution of hexane and acetone. **1** and **2** crystallize in the monoclinic $P2_1/c$ and $P2_1/n$ space groups as blocks and as prisms respectively. The ruthenium centers in **1** and **2** are co-ordinated to the bidentate Schiff base, to a chloride atom, and to the arene ring to give a pseudo-octahedral geometry around them. The whole arrangement is referred to as the familiar three-legged piano stool in which the Schiff base and the Cl atom serve as the base while the arene ring serve as the apex of the stool. Polymorph **2** has an acetone molecule in the asymmetric unit. Of interest is the similar behavior of the solvate on heating which shows the crystals shuttering at about 531.6 and 523.4 K for **1** and **2** respectively.

1. Introduction

Polymorphism can be defined as the occurrence of different crystal structures of the same chemical entity [1]. When the different crystal systems of a substance are as a results of hydration or solvation, then the phenomenon is referred to as solvato-morphism [2], a feature that is of important in pharmaceuticals. Many pharmaceutical solids can exist in different physical forms such as polymorphs or solvato-polymorphs and can exhibit differences in chemical and physical properties. These properties directly impact on pharmaceuticals stability, dissolution and bioavailability and also on intellectual property issues [3]. Detailed literature on polymorphism in organic molecules is available [2,3]. However, literature on polymorphism of organometallic compounds often used as catalysts precursors and intermediates in several homogeneous and heterogeneous processes [4–6], has not received much attention.

Half-sandwich organo–ruthenium complexes have gained interest in catalytic organic transformations such as transfer hydrogenation, alkene polymerization, ring opening metathesis and olefin oxidation [7,8]. In addition ruthenium complexes with *N, N'*-bidentate ligands have also been studied as anticancer agents [9,10]. Of interest in these organometallic arene ruthenium complexes, is the pseudo-octahedral coordination environment around the metal center where three coordination sites of the metal are often occupied by an aromatic ring in a η^6-manner while other ligands occupy the other three coordination sites [11,12]. This makes the properties of arene ruthenium complexes to be easily tailored by modification of the arene rings and/or the coordinating ligands [8]. In this paper we report the synthesis and structural characterization of $[(\eta^6\text{-}C_6H_6)RuCl(C_5H_4\text{-}2\text{-}CH{=}N\text{-}R)]PF_6$, **1** and its acetone solvate **2** as solvato-polymorphs obtained using different crystallization methods.

2. Experimental

2.1. Materials and methods

All manipulations were carried out under nitrogen atmosphere using Schlenk line techniques. All reagents and solvents were purchased from commercial sources (Sigma–Aldrich). Solvents were dried using standard techniques and stored over 4 Å

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molecular sieves. NMR spectra were recorded on a Bruker topspin 400 MHz spectrometer. Deuterated solvent DMSO-d_6 (Aldrich) was used as purchased. Melting points were measured on an Ernest Leitz Wetzlar hot stage microscope. Elemental analyses were performed on Thermal-Scientific Flash 2000 CHNS/O analyzer. Infrared spectra were recorded using an ATR Perkin Elmer Spectrum 100 spectrophotometer between 4000 and 400 cm^{-1} in the solid state. Mass spectra were recorded via Waters Micromass LCT Premier TOF-MS and ESI in the positive mode. DSC measurements was recorded on a Universal V4.7A TA instrument using nitrogen at a flow rate of 10 ml/min. Ruthenium trichloride was received from DLD-scientific. The Ru (II)-arene dimeric precursor [Ru [(η6-C_6H_6) Ru(μ-Cl)Cl]$_2$ was synthesized according to reported literature procedures [13] and the imino-pyridine ligands prepared following reported literature procedures [14].

2.2. Synthesis

The complexes were prepared using a modified method from Gomez et al. [15]. To a suspension of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ (0.2 mmols) in methanol (20 ml) was added the ligand (0.42 mmols). The mixture was stirred at room temperature for 3 h followed by the reduction in the volume of the solvent *in vacuo* to about (10 ml) before adding NH_4PF_6 (0.42 mmol). The mixture was then cooled in an ice bath while stirring for 2 h leading to a precipitate which was collected by filtration. The filtrate was washed with diethyl ether and dried *in vacuo*.

Yield (89%) m.p. 248 (decomp.). ^{1}H NMR (400 MHZ, DMSO-d_6, 25 °C). δ = 9.67 (s, 1H, py); δ = 8.88 (s, 1H, CH═N); δ = 8.32 (d, 1H, py), δ = 8.21 (d, 1H, py); δ = 8.19 (s, 1H, py); δ = 7.93 (m, 1H, py); δ = 7.34 (m, 3H, Ar); δ = 5.87 (s, 6H, C_6H_6); δ = 2.37 (s, 3H, Ar-CH_3), δ = 2.17 (s, 3H, Ar-CH_3). ^{13}C NMR (400 MHZ, DMSO-d^6, 25 °C) δ = 173.59 (CH═N), δ = 156.24 (py); δ 153.95 (py), δ = 150.96 (py); δ = 140.12 (py); δ = 131.12 (Ar); δ = 130.03 (Ar); δ = 129.3 (Ar); δ = 128.99 (Ar); δ = 128.7(Ar); δ = 128.23 (Ar); δ = 87.21 (C_6H_6); δ = 19.75 (Ar-CH_3), δ = 18.11 (Ar-CH_3). Calcd for [$C_{20}H_{20}ClN_2Ru$]PF_6 C, 42.15; H, 3.54; N, 4.92. Found: C, 42.11; H, 3.70; N, 5.03. MS (ESI, M/Z): 425.0363 for [$C_{20}H_{20}ClN_2Ru$] $^+$

2.3. X-ray crystallography

Crystals of **1** suitable for single crystal X-ray diffraction studies were grown by the liquid diffusion method in which the solutions of the compounds in acetone were layered with hexane and left undisturbed for 2 days. The crystals for the complex **2** were grown by the slow evaporation of its acetone solution. Crystal evaluation and data collection were performed on a Bruker Smart *APEX II* diffractometer with Mo Kα radiation (k = 0.71073 Å). The reflections were successfully indexed by an automated indexing routine built in the *APEXII* program suite [16]. The final cell constants were calculated from a set of 6460 strong reflections from the actual data collection. Data reduction was carried using the program *SAINT*$^+$ [16]. The structure was solved by direct methods using *SHELXS* [17] and refined [17]. All structures were checked for solvent-accessible cavities using *PLATON* [17]. Non-H atoms were first refined isotropically and then by anisotropic refinement with full-matrix least-squares calculations based on F^2 using *SHELXS* [17]. All H atoms were positioned geometrically and allowed to ride on their respective parent atoms. The carboxyl H atoms were located from the difference map and allowed to ride on their parent atoms. All H atoms were refined isotropically. The absorption correction was based on fitting a function to the empirical transmission surface as sampled by multiple equivalent measurements [17]. Crystal data and structure refinement information for compounds **1** and **2** are summarized in Table 1.

3. Results and discussion

3.1. Synthesis

The mononuclear iminopyridyl ruthenium complex [Ru(η^6-C_6H_6)[[L]Cl]PF_6 (L = 2,6-dimethyl-phenyl-pyridin-2-ylmethylene amine) was synthesized by the reaction of [(η^6-C_6H_6)Ru(μ-Cl)Cl]$_2$ with 2, 6-dimethyl-*N*-(pyridin-2-ylmethylene) aniline in methanol at room temperature. The complex was isolated using hexaflourophosphate as the counter ion as an air stable yellow (in the web version) solid. As mentioned earlier the crystals of **2**, were obtained by recrystallization of **1** from an acetone/hexane solution. The crystal morphologies of the two were different in that crystals of polymorph **1** were blocks while those of polymorph **2** were prisms (Fig. 1).

The complex formation was confirmed using ^{1}H and ^{13}C NMR by following the chemical shift of the imine proton of the ligand and complex. A downward shift from 8.88 to 8.00 ppm of the imine proton of the free ligand was observed confirming coordination of the imine nitrogen to the ruthenium center. The downward shift in the imine proton upon coordination can be due to the π-back-bonding from ruthenium to the imine bond and/or due to conformational changes experienced by the ligand in order to facilitate coordination of the imine nitrogen to the ruthenium center [18]. In the ^{13}C NMR spectra of all the complexes, the −CH═N carbon shifts up field for the complex as compared to the uncoordinated pyridine-imine ligand. This is probably due to a deshielding effect caused by increased charge transfer between the imine nitrogen and the ruthenium metal. The cationic complexes also display a septet in the ^{31}P NMR spectra for the cation PF_6, in the range of −131 to −151 ppm, which agrees with the literature values for other hexaflourophosphate salts [19].

The imine bond stretching frequency of the ligands in IR spectroscopy shifted from higher (1638.0 cm^{-1}) in the ligands to lower wavenumbers of 1614.0 cm^{-1} in the complex. This decrease in stretching frequency is due to sigma donation of electrons from the imine nitrogen to the ruthenium center, thus resulting in less double bond character of the imine bond. In addition the IR spectra of the complexes exhibit strong bands at around 826 cm^{-1} due to the stretching P−F mode of the counter ion of these complexes. The ESI mass spectra of the compounds **1** showed a peak associated with the loss of the PF_6 counter ions.

3.2. Thermal analysis

DSC traces of **1** and **2** done between 298 K and 873 K are given in Fig. 2. The trace of **1** showed two endotherms while that for **2** showed three endotherms. For both solvato-polymorphs there seems to be phase changes at 531.6 and 523.4 K respectively followed by decomposition at 639.0 and 638.2 K (Table 2). For compound **2** an endotherm at 400.7 K attributed to the loss of the acetone was observed with a heat of loss of about 265.5 kJ mol^{-1}, probably is a rearrangement of compound **1**. There seems to be possible phase change in the structures of **1** and **2** leading to shuttering of the crystals, observed at 531.6 and 523.4 K corresponding to enthalpies of 179.8 kJ mol^{-1} for **1** and 5.6 kJ mol^{-1} for **2**. It's not clear if the difference in the enthalpy changes can be attributed to the relative stabilities of the two solvato-polymorphs at this stage. A similar trend was also observed for the enthalpies associated with decompositions, 15.2 kJ mol^{-1} and 5.5 kJ mol^{-1} for polymorph **1** and **2**, even though they occur at very close temperatures, 639.0 and 638.2 K, respectively. The difference in the two energies could be associated to the differences in the packing of molecules in the crystals and also intermolecular interactions between the molecules in the solid state. The trace for compound **1**

Table 1
Summary of the crystal data of 1 and 2.

Compound	1	2
Formula	$C_{20}H_{20}ClF_6N_2PRu$	$C_{23}H_{26}ClF_6N_2OPRu$
Formula weight	569.87	627.95
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a, Å	11.6810(11)	9.0080(4)
b, Å	15.4988(14)	19.6320(9)
c, Å	12.8615(12)	14.3950(8)
α, °	90	90
β, °	114.971(2)	106.3140(10)
γ, °	90	90
V, Å^3	2110.8(3)	2443.2(2)
Z	4	4
ρ_{calcd}, Mg/m^3	1.793	1.707
T, K	173(2)	173(2)
Theta range for data collections, °	1.923 to 27.563	1.802 to 28.858
λ, Å	0.71073	0.71073
F (000)	1136	1264
Crystal size, mm^3	0.252 × 0.225 × 0.160	0.430 × 0.317 × 0.192
No. of reflections collected	30,334	19,913
No of independent reflections.	4546[R(int)] = 0.0282]	5556[R(int)] = 0.0159]
Goodness-of-fit on F^2	1.091	0.940
Final R indices	0.0193, 0.0539	0.0285, 0.0788
R indices (all data)	0.0253, 0.0562	0.0298, 0.0805
Largest diff.peak& hole, e.Å^{-3}	0.513 & −0.837	0.761 & −0.771

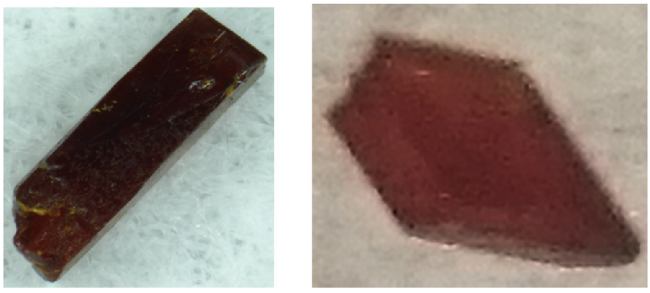


Fig. 1. Morphologies of the two polymorphic forms: (1) blocks (2) Prisms.

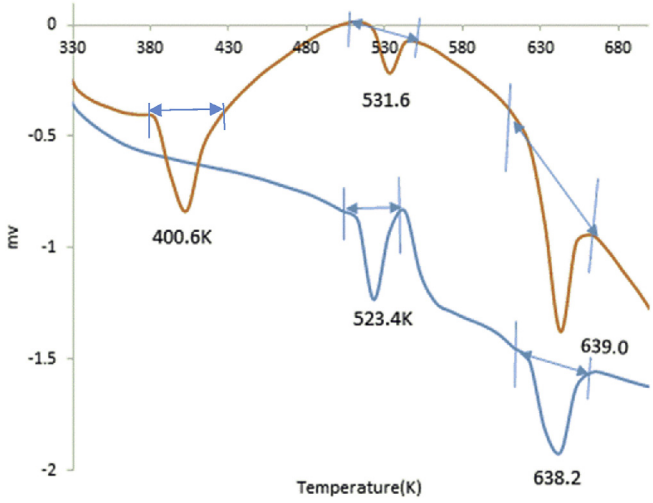


Fig. 2. : DSC traces of compound 1 (in brown) and 2 (in blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

exhibited possible heat losses between 523.4 after the shattering of the crystals, and 638.3 K, the decomposition temperature.

3.3. Molecular and crystal structure analysis

The molecular structures of complexes **1** and **2** (Figs. 3 and 4) are similar and have a Ru center in a pseudo-octahedral geometry and coordinated by the *N,N*-bidentate ligand and Cl atom and also to C atoms of an arene ring. The two N atoms and the Cl atom form the legs while the arene ring forms the seat of what is normally referred to as a "three legged piano stool". The asymmetric units are however different where in **2** an acetone molecule is also present in addition to the piano stool, $[(\eta^6\text{-}C_6H_6)RuCl(L)]^+$ and a molecule of PF_6 as a counter anion. The two complexes have two major planes defined the pyridine ring and the six member metallacycle, and by the 2, 6-dimethyl substituted phenyl ring. The dihedral angles between the two sets of planes are 74.9 (1)° and 83.2 (1)° in complexes **1** and **2** respectively. An overlay of the two cationic species in complexes **1** and **2** shows just a slight tilt in the plane containing the pyridinyl moiety with a root mean square value of only 0.0912 Å (Fig. 5).

The Ru–N bond distances are similar in both complexes lie between 2.0687(12) and 2.0914(18) Å and are similar to those reported for similar arene–ruthenium complexes with *N, N'*-donor ligands [20] as well as those of half-sandwich ruthenium complexes [21]. The N–Ru–N bond angles lie between 76.54(7) and 76.92(8) ° while N–Ru–Cl bond angles lie between 81.93(6) and 88.91(5) ° (Table 3).

The crystal densities can be used to indicate the stability of polymorphs especially for temperature dependent polymorphs [22]. However, in this case solvato-polymorph **1** has a slightly higher density than **2** by 0.086 M gm^{-3} showing that packing in **2** is probably affected by the presence of acetone molecule in its crystal structure (Fig. 6).

C–H … Cl and C–H … F intermolecular interactions play a role in the crystal packing of the two solvato-polymorphs 1 and 2 (Table 4). In both polymorphs 1 and 2 the chloride ion is involved in C–H … Cl intermolecular interactions while the fluorine atoms of the counter anion contribute to C–H … F intermolecular interactions (Table 4).

Table 2
Thermodynamic data obtained from DSC curves of 1 and 2.

	T_{trs} (K)	$\Delta_{trs}H$ (kJ mol^{-1})	T_{trs} (K)	$\Delta_{trs}H$ (kJ mol^{-1})	T_{trs} (K)	$\Delta_{trs}H$ (kJ mol^{-1})
1			523.4	179.8	638.2	266.4
2	400.7	265.5	531.6	5.5	639.0	294.9

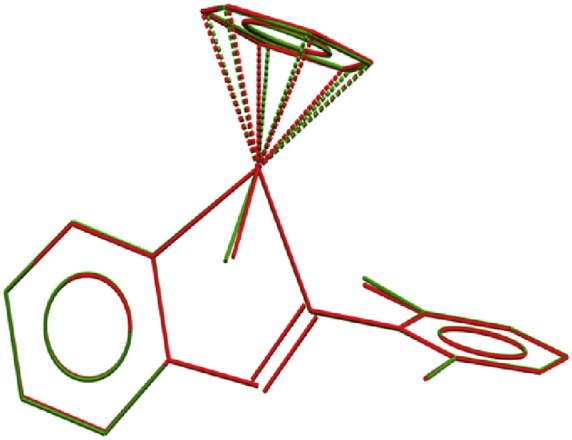


Fig. 3. Overlay of polymorhs 1 and 2 with r.m.s. deviation of 0.0912 Å

4. Conclusion

The structure of the two solvato-polymorphs of the title compound [(η^6-C_6H_6)RuCl(C_5H_4-2-CH=N-R]PF_6, where R = 2,6-$(CH_3)_2C_6H_3$) were structurally determined using ^{1}H and ^{13}C NMR and as well as single crystal X-ray diffraction. Compound **1** had a slightly higher density than that of **2** whose density is compromised by the presence of the acetone molecule in the crystal structure. Thermal analysis showed interesting results in which the enthalpies associated with possible structural changes and with decomposition seemed notably different (higher in **1** than in **2**). Acetone does not seem to play a role in the intermolecular interactions in **2** as no notable intermolecular interactions were observed involving the O atom and perhaps just fills the voids formed on crystallization of **2**.

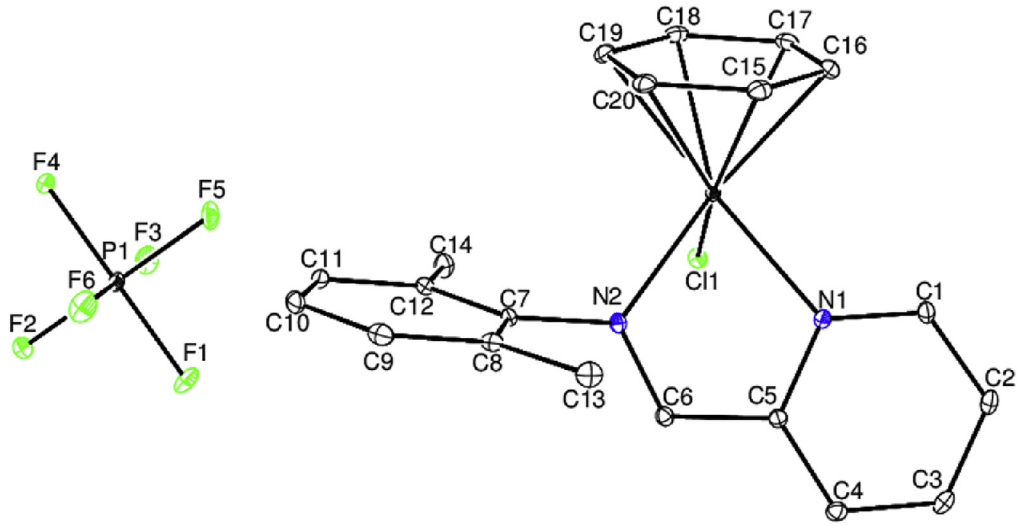


Fig. 4. Molecular structure of 1 with ellipsoid displacement drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

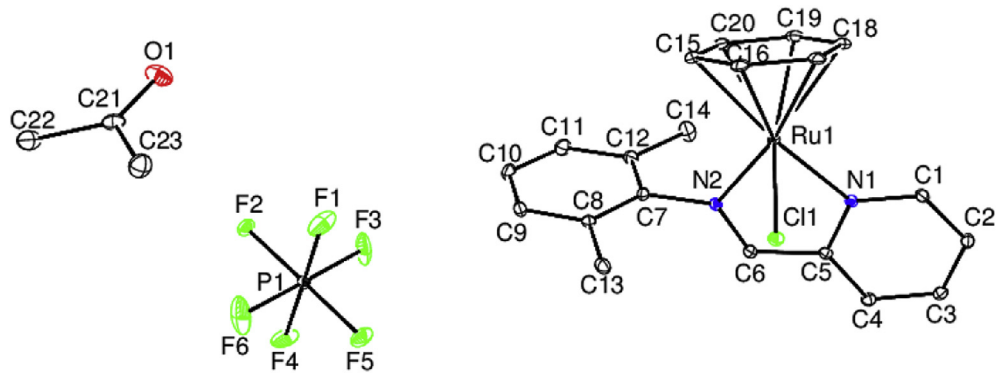
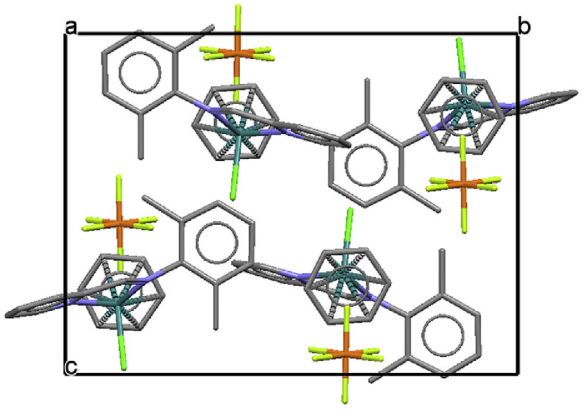


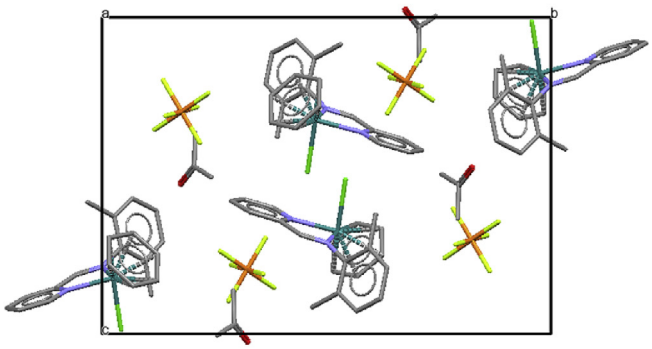
Fig. 5. Molecular structure of 2 with ellipsoid displacement drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 3
Selected bond lengths (Å) and angles (deg°) 1 and 2.

	1	2		1	2
Bond distances (Å)					
Ru—N_{Py}	2.0799(12)	2.0914(18)	Ru—Cl	2.3910(4)	2.3992(5)
N_{amine}—C_{amine}	1.3642(18)	1.452(2)	N_{amine}—C_{Ph}	1.4310(18)	1.358(3)
Ru—N_{amine}	2.0687(12)	2.0904(16)			
Bond angles (°)					
N(3)-Ru(1)-N(2)	76.54(7)	76.92(8)	N(3)-Ru(1)-Cl(1	82.71(5)	88.91(6)
N(2)-Ru(1)-Cl(1)	88.73(5)	81.93(6)			



1



2

Fig. 6. Packing of polymorph 1 and packing of polymorph 2 as viewed down the crystallographic b axis.

Table 4
Hydrogen bonding interactions in the crystal structures of 1 and 2.

D—H … A	D—H	H … A	D … A	<D—H…A	Symmetry code
1					
C(1)—H(1) … Cl(1)	0.95	2.75	3.525(2)	139	-x + 1, -y + 2, -z
C(2)—H(2) … F(4)	0.95	2.37	3.294(2)	163	x, y + 1, z
C(4)—H(4) … F(6)	0.95	2.54	3.384(2)	148	-x + 2, y + ½, -z + ½
C(6)—H(6) … F(6)	0.95	2.60	3.417(3)	150	-x + 2, y + ½, -z + ½
2					
C(1)—H(1) … Cl(1)	0.95	2.83	3.692(2)	152	-x + 1, -y + 2, -z
C(6)—H(6) … F(2)	0.95	2.32	3.235(3)	161	x, y + 1, z
C(22)—H(22A) … F(3)	0.98	2.61	3.498(3)	151	-x + 2, y + ½, -z + ½
C(1)—H(1) … Cl(1)	0.95	2.83	3.692(2)	152	-x + 2, y + ½, -z + ½

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Supplementary material

CCDC 1443621 and 1443622 contain the supplementary crystallogarphic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html or the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223336033).

References

[1] F.H. Herbstein, Cryst. Growth Des. 4 (2004) 1419.
[2] (a) H.G. Brittain, J. Pharm. Sci. 101 (2012) 464;
(b) G.M. Lombardo, F. Punzo, J. Mol. Struct. 1078 (2014) 158;
(c) J. Ruiz, V. Rodriguez, N. Cutillas, A. Hoffmann, A.-C. Chamayou, K. Kazmierczak, C. Janiak, CrystEngComm 10 (2008) 1928.
[3] A. Bacchi, G. Cantoni, P. Pelagatti, Cryst. Eng. Comm. 15 (2013) 6722.
[4] D. Braga, F. Grepioni, Chem. Soc. Rev. 29 (2000) 229.
[5] A. Zeller, G. Eickerling, E. Herdtweck, M.U. Schmidt, T. Strassner, J. Organomet. Chem. 692 (2007) 4725.
[6] E.A. Nyawade, H.B. Friedrich, C.M. M'thiruaine, B. Omondi, J. Mol. Struct. 1048 (2013) 426.
[7] P. Kumar, A.K. Singh, R. Pandey, P.-Z. Li, S.K. Singh, Q. Xu, D.S. Pandey, J. Organomet. Chem. 695 2205.
[8] A.K. Singh, D.S. Pandey, Q. Xu, P. Braunstein, Coord. Chem. Rev. 270–271 (2014) 31.
[9] Y.N. Vashisht Gopal, N. Konuru, A.K. Kondapi, Archives Biochem. Biophys. 401 (2002) 53.
[10] R.E. Morris, R.E. Aird, P. del Socorro Murdoch, H. Chen, J. Cummings, N.D. Hughes, S. Parsons, A. Parkin, G. Boyd, D.I. Jodrell, P.J. Sadler, J. Med. Chem. 44 (2001) 3616.
[11] S.S. Keisham, Y.A. Mozharivskyj, P.J. Carroll, M.R. Kollipara, J. Organomet. Chem. 689 (2004) 1249.
[12] S. Gloria, G. Gupta, V. Rao Anna, B. Das, K.M. Rao, J. Coord. Chem. 64 (2011) 4168.
[13] M.A. Bennett, A.K. Smith, J. Chem. Soc. Dalton Trans. (1974) 233.
[14] H. Hu, L. Zhang, H. Gao, F. Zhu, Q. Wu, Chem. Eur. J. 20 (2014) 3225.
[15] J. Gómez, G. García-Herbosa, J.V. Cuevas, A. Arnáiz, A. Carbayo, A. Muñoz, L. Falvello, P.E. Fanwick, Inorg. Chem. 45 (2006) 2483.
[16] Bruker-AXS, Bruker-AXS, Madison, Wisconsin, USA, 2009.
[17] G. Sheldrick, Acta Cryst. Sec. A 64 (2008) 112.
[18] L.C. Matsinha, S.F. Mapolie, G.S. Smith, Polyhedron 53 (2013) 56.
[19] A.R. Burgoyne, B.C.E. Makhubela, M. Meyer, G.S. Smith, Eur. J. Inorg. Chem. 2015 (2015) 1433.
[20] R. Lalrempuia, M. Rao Kollipara, Polyhedron 22 (2003) 3155.
[21] (a) P. Singh, A.K. Singh, Organometallics 29 (2010) 6433;
(b) T. Bugarcic, A. Habtemariam, R.J. Deeth, F.P.A. Fabbiani, S. Parsons, P.J. Sadler, Inorg. Chem. 48 (2009) 9444;
(c) M.L. Soriano, F.A. Jalón, B.R. Manzano, M. Maestro, Inorg. Chim. Acta 362 (2009) 4486.
[22] (a) A. Burger, R. Ramberger, Mikrochim. Acta 2 (1979) 273;
(b) A. Burger, R. Ramberger, Mikrochim. Acta 2 (1979) 259.