Acta Cryst E
CRYSTALLOGRAPHIC
COMMUNICATIONS

ISSN 2056-9890

Crystal structure of *fac*-aqua[(*E*)-4-(benzo[*d*]thiazol-2-yl)-*N*-(pyridin-2-ylmethylidene)aniline-κ^2N,N']tricarbonylrhenium(I) hexafluoridophosphate methanol monosolvate

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Received 13 March 2019
Accepted 29 March 2019

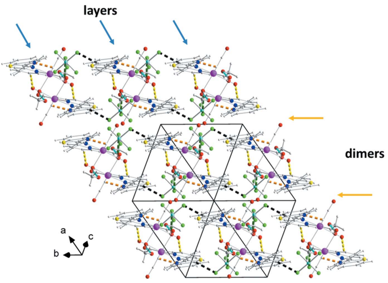
Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; tricarbonyl rhenium (I); mixed ligand complex; 2-(4′-aminophenyl)benzothiazole; *trans* effect; Hirshfeld surface analysis.

CCDC reference: 1906503

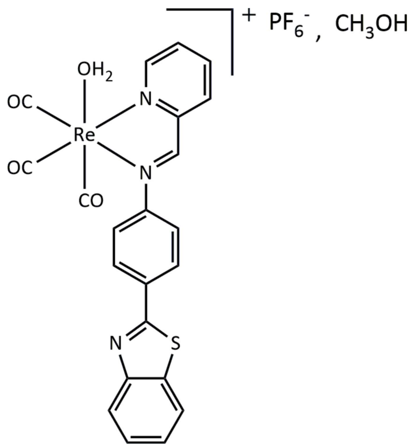
Supporting information: this article has supporting information at journals.iucr.org/e

In the title compound, *fac*-$[Re(C_{19}H_{13}N_3S)(CO)_3(H_2O)]PF_6\cdot CH_3OH$, the coordination environment of the Re^I atom is octahedral with a C_3N_2O coordination set. In this molecule, the *N*,*N*′ bidentate ligand, (*E*)-4-(benzo[*d*]thiazol-2-yl)-*N*-(pyridin-2-ylmethylidene)aniline, and the monodentate aqua ligand occupy the three available coordination sites of the $[Re(CO)_3]^+$ core, generating a ‘2 + 1’ mixed-ligand complex. In this complex, the Re—C bonds of the carbonyl ligands *trans* to the coordinating *N*,*N*′ atoms of the bidentate ligand are longer than the Re—C bond of the carbonyl group *trans* to the aqua ligand, in accordance with the intensity of their *trans* effects. The complex is positively charged with PF_6^- as the counter-ion. In the structure, the complexes form dimers through π–π intermolecular interactions. O—H···O and O—H···N hydrogen bonds lead to the formation of stacks parallel to the *a* axis, which further extend into layers parallel to $(0\bar{1}1)$. Through O—H···F hydrogen bonds between the complexes and the PF_6^- counter-anions, a three-dimensional network is established.



1. Chemical context

‘2 + 1’ mixed-ligand complexes of general formula *fac*-$[M(CO)_3L_1L_2]$, where M is Re or ^{99m}Tc, L_1 is a bidentate ligand (bipyridine, 2-picolinic acid, acetylacetone, *etc*) and L_2 is a monodentate ligand (aqua, imidazole, phosphine or isocyanide), have been studied extensively for the development of novel radiopharmaceuticals for diagnosis (M = ^{99m}Tc) or radiotherapy (M = $^{186/188}$Re) (Knopf *et al.*, 2017; Mundwiler *et al.*, 2004; Papagiannopoulou *et al.*, 2014; Triantis *et al.*, 2013; Shegani *et al.*, 2017). Furthermore, recent studies have revealed the potential of such *fac*-$[Re(CO)_3L_1L_2]$ complexes as anticancer agents (Leonidova & Gasser, 2014). According to the ‘2 + 1’ strategy, the intermediate aqua complex *fac*-$[Re(CO)_3(L_2)(H_2O)]$ plays a crucial role. The labile water ligand can readily be substituted by a monodentate ligand L_2 (typically heterocyclic aromatic amines, isocyanides, phosphines), generating the final *fac*-$[Re(CO)_3L_2L_1]$ product in high yield. The ‘2 + 1’ complexes are characterized by kinetic stability and structural variability that facilitates the tuning of physicochemical properties and tethering of pharmacophores of interest towards the generation of targeted multifunctional compounds.



As part of our ongoing research in the field of Re/Tc coordination chemistry, we report herein the structure of the '2 + 1' tricarbonyl rhenium(I) complex *fac*-[Re(CO)$_3$-(NNbz)(H$_2$O)]PF$_6$·CH$_3$OH where the bidentate NNbz ligand is (*E*)-4-(benzo[*d*]thiazol-2-yl)-*N*-(pyridin-2-ylmethylidene)-aniline. The NNbz ligand carries the 2-(4′-aminophenyl)-benzothiazole scaffold, which also exhibits interesting biological properties against a variety of targets and presents great potential for diagnostic/therapeutic applications (Keri *et al.*, 2015; Kiritsis *et al.*, 2017; Bradshaw & Westwell, 2004).

2. Structural commentary

The asymmetric unit of the title compound comprises one *fac*-aquatricarbonyl-(*E*)-4-(benzo[*d*]thiazol-2-yl)-*N*-(pyridin-2-ylmethylidene)aniline–rhenium(I) complex molecule, one PF$_6^-$ counter-anion and one methanol solvent molecule (Fig. 1). Within the complex, the Re^I atom presents a distorted octahedral C$_3$N$_2$O coordination set with the three tricarbonyl ligands in facial and the bidentate diimine (NNbz) and the monodentate water ligands in a *cis* arrangement (Fig. 1). The two coordinating nitrogen atoms N1 and N2 of the bidentate NNbz ligand together with two carbonyl carbon atoms define the equatorial plane with almost perfect planarity (deviation from the least-squares plane = 0.006 Å). The Re—N1 and Re—N2 distances are 2.177 (2) and 2.194 (2) Å, respectively. The oxygen atom of the water molecule [Re—O1*W* = 2.189 (2) Å] and the carbon atom from the third carbonyl ligand define the axial direction of the octahedron. Both the Re—N and the Re—O distances fall in the range of observed values in complexes with a diimine, aqua or tricarbonyl core (Mella *et al.*, 2016; Connick *et al.*, 1999; Schutte *et al.* 2011; Salignac *et al.*, 2003; Knopf *et al.*, 2017; Rillema *et al.*, 2007; Barbazán *et al.*, 2009; Carrington *et al.*, 2016; Tzeng *et al.*, 2011; Grewe *et al.*, 2003). The NNbz ligand deviates from planarity as the dihedral angle between the central phenyl ring and the benzothiazole group is 20.48 (8)°, while the dihedral angle between the phenyl ring and the pyridine ring is 39.13 (8)°.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O2^{i}	0.91 (4)	2.59 (4)	3.439 (4)	156 (3)
C9—H9···F3^{ii}	0.94 (3)	2.47 (3)	3.390 (3)	166 (2)
O1*W*—H101···O1*M*	0.91 (4)	1.67 (4)	2.558 (3)	165 (4)
O1*W*—H102···F1	0.72 (4)	2.36 (4)	3.059 (5)	164 (4)
O1*M*—H201···N3^{iii}	0.88 (5)	2.01 (5)	2.842 (3)	158 (4)

Symmetry codes: (i) $-x+1, -y+2, -z+2$; (ii) $-x+1, -y+1, -z+2$; (iii) $-x+2, -y+1, -z+1$.

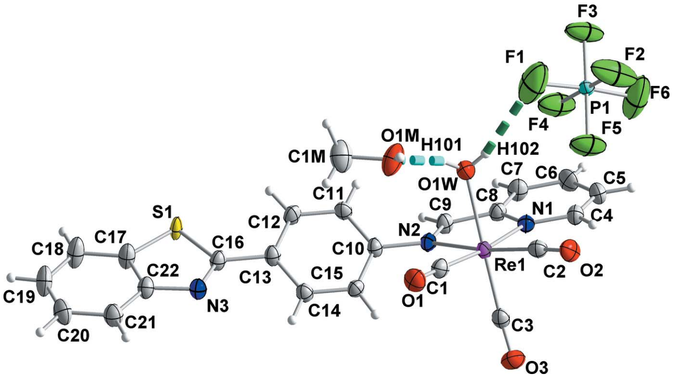


Figure 1
Molecular structure and labeling scheme for the title Re^I complex, the methanol solvent molecule and the PF$_6^-$ counter-anion. Displacement ellipsoids are drawn at the 50% probability level. Cyan and dark-green dashed lines indicate the O1*W*—H101···O1*M* and O1*W*—H102···F1 hydrogen bonds, respectively.

3. Supramolecular features

The counter-anion and the methanol solvent molecules form O1*W*—H102···F1 and O1*W*—H101···O1*M* hydrogen bonds with the aqua ligand (Fig. 1, Table 1). Neighbouring complexes present a π–π overlap between their coordinating NNbz ligands, forming dimers (Fig. 2). More specifically, the mol-

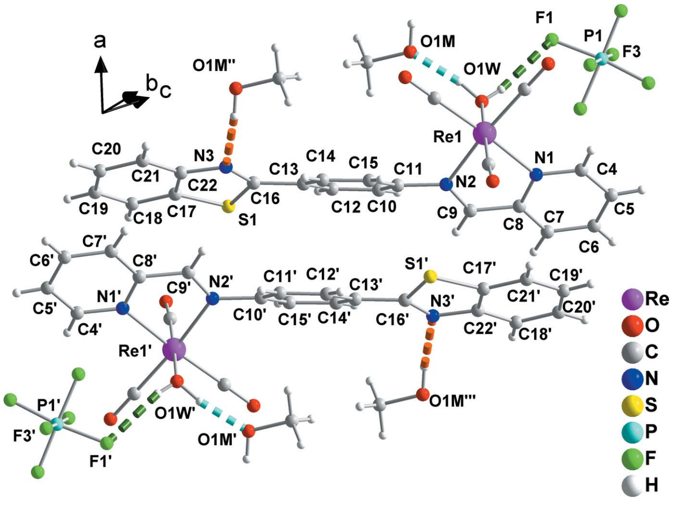


Figure 2
Dimers of complexes formed through π–π overlap between their coordinating NNbz ligands and intermolecular interactions between dimers with methanol solvent molecules and PF$_6^-$ counter-anions. Colour code as in Fig. 1 with the additional O1*M*—H201···N3 interactions indicated by orange dashed lines. [Symmetry codes: (′) $1-x, 1-y, 1-z$; (″) $2-x, 1-y, 1-z$; (‴) $-1+x, y, z$.]

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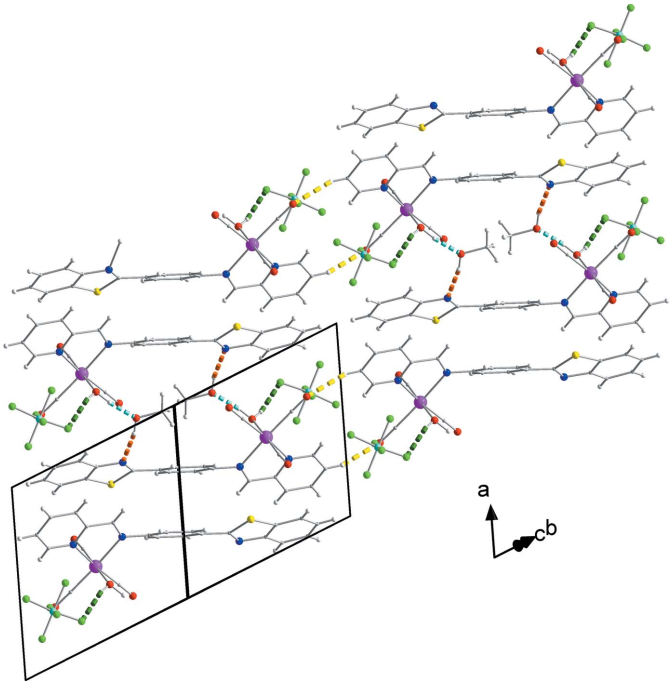

Figure 3
Layers of complexes parallel to $(0\bar{1}1)$. C5—H5···O2 hydrogen bonds are indicated by yellow dashed lines. For the atoms and the rest of the bonds, the colour code is as in Fig. 2.

ecules are centrosymetrically related and thus exhibit parallel phenyl rings of the NNbz ligand at a distance of 3.50 (1) Å. In addition, both the pyridine rings and the phenyl rings of the benzothiazole parts of neighbouring centrosymmetrically related NNbz ligands overlap with each other, with their respective centroids *Cg*1 and *Cg*2 lying at a distance of 3.8525 (1) Å and forming an angle of 18.67 (6)° [*Cg*1 and *Cg*2′ are the centroids of the N1, C4–C8 and C17′–C22′ rings; symmetry code: (′) $1 - x, 1 - y, 1 - z$; Fig. 2]. The dimers are stacked along the *a*-axis direction. Methanol solvent molecules are interleaved between adjacent dimers within the stacked molecules and are linked through intermolecular O1*W*—H101···O1*M* and O1*M*—H201···N3 interactions (Fig. 3). These stacks are extended into layers parallel to $(0\bar{1}1)$ through C5—H5···O2 hydrogen bonds and further O1*W*—H102···F1, C9—H9···F3$^{\rm ii}$ (Table 1) hydrogen bonds between the counter-anions and the coordinating ligands result in the formation of a three-dimensional network structure (Fig. 4).

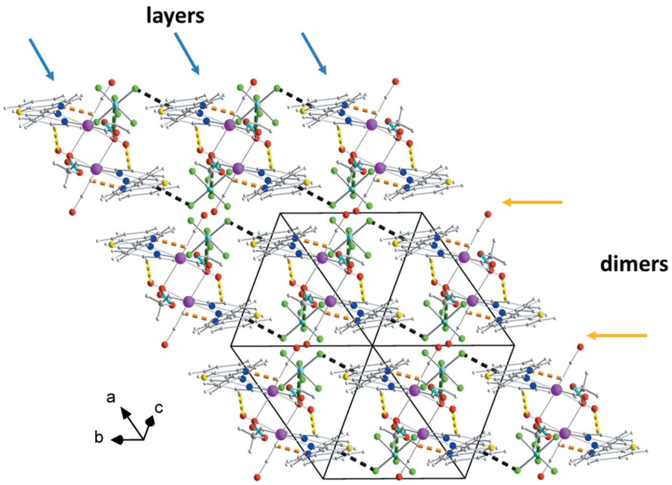

Figure 4
Three-dimensional arrangement of layers. C9—H9···F3$^{\rm ii}$ hydrogen bonds are indicated by black dashed lines. For the atoms and the rest of the bonds, the colour code is as in previous figures. The cyan arrows indicate the position of the layers within the structure and the orange ones the areas where the complexes interact through π–π interactions.

4. Hirshfeld surface study

The view of the Hirshfeld surface mapped with $d_{\rm norm}$ (Fig. 5*a*) reveals almost all of the hydrogen-bonding interactions discussed above as intense red areas. The same view of the surface mapped with the curvedness property reveals the contact areas of the tricarbonyl part of the complex with the benzothiazole end of the coordinating ligand, as indicated by patches of the same shape (circled areas in Fig. 5*b*). Finally, the plot of the surface mapped with the shape-index property (Fig. 5*c*) gives clear evidence that this part of the molecule interacts with a centrosymmetrically related neighbour, as the shape of the patterns on the surface are related centrosymmetrically. The rhombic and triangular shapes with the complementary red(hollows)/blue(bumps) colours are characteristic of π–π interactions. The asymmetric distribution of

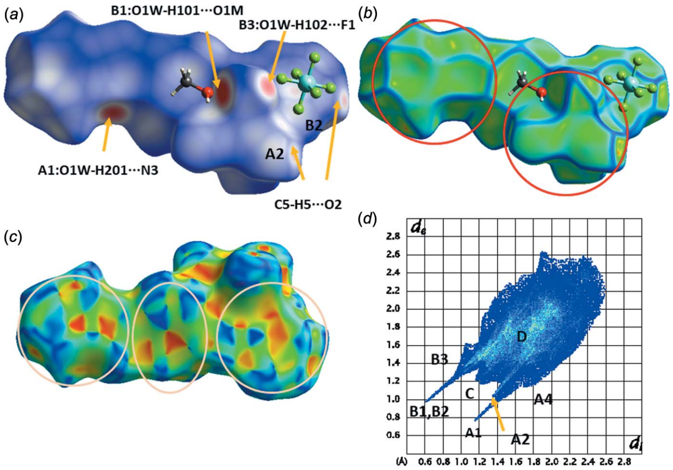

Figure 5
Views of the Hirshfeld surfaces mapped over (*a*) $d_{\rm norm}$, (*b*) curvedness and (*c*) shape-index, and (*d*) the fingerprint plot for the title complex. The red circles in (*b*) indicate patches of the same shape corresponding to contact areas of neighbouring complexes. The central ellipse in (*c*) indicates the π–π overlap of the central phenyl rings, and the two circles at both ends of the surface the overlap of the pyridine ring and the phenyl ring of the benzothiazol part of neighbouring centrosymmetrically related NNbz ligands. In (*d*), $d_{\rm e}$ and $d_{\rm i}$ are the distances to the nearest atom centre exterior and interior to the surface. A1 and A4 stand for the acceptor atoms in O1*W*—H201···N3 and C···H interactions. A2, B2 indicate the acceptor atom and the H-donated atom in the C5—H5···O2 interaction, B1 the H101 atom in the O1*W*—H101···O1*M* interaction, and B3, C and D the H···F, H···H and C···C interactions, respectively.

Table 2
Characteristic bond lengths (Å) for a series of Re^I complexes with a *fac*-aqua tricarbonyl diimine octahedral core.

	Re—N1	Re—C1	Re—N2	Re—C2	Re—O1*W*	Re—C3
Present work	2.177 (2)	1.925 (3)	2.194 (2)	1.920 (3)	2.189 (2)	1.899 (3)
ENAJAG[a]	2.156 (7)	1.935 (11)	2.165 (7)	1.884 (10)	2.176 (7)	1.886 (11)
ENAJEK[a]	2.173 (5)	1.911 (7)	2.178 (5)	1.921 (7)	2.191 (5)	1.879 (7)
FIWQUX-1[b]	2.168 (7)	1.91 (1)	2.180 (5)	1.914 (8)	2.215 (6)	1.88 (1)
FIWQUX-2[b]	2.164 (7)	1.902 (10)	2.178 (7)	1.909 (10)	2.210 (6)	1.868 (10)
KAWLO*L*[c]	2.168 (4)	1.914 (6)	2.175 (4)	1.929 (7)	2.162 (3)	1.893 (5)
UHUNOA[d]	2.161 (5)	1.938 (7)	2.183 (5)	1.931 (7)	2.181 (5)	1.898 (7)
	2.160 (5)	1.928 (6)	2.174 (4)	1.926 (9)	2.196 (6)	1.915 (7)
SEHGUK[e]	2.210 (3)	1.928 (4)	2.200 (3)	1.929 (4)	2.196 (2)	1.896 (4)
PIDYILf[f]	2.167 (2)	1.918 (3)	2.167 (2)	1.918 (3)	2.143 (3)	1.912 (4)
UHUNUG[d]	2.161 (6)	1.901 (9)	2.165 (6)	1.914 (10)	2.190 (5)	1.882 (10)
	2.165 (6)	1.901 (9)	2.161 (6)	1.91 (1)	2.190 (5)	1.88 (1)
VUDWAT[g]	2.185 (4)	1.888 (7)	2.175 (6)	1.925 (8)	2.165 (5)	1.853 (9)
ETEDEO[h]	2.186 (5)	1.933 (6)	2.178 (5)	1.902 (7)	2.155 (5)	1.896 (7)
IZORIZ[i]	2.203 (3)	1.912 (4)	2.142 (3)	1.922 (4)	2.173 (3)	1.904 (4)
TUTDAN[j]	2.168 (6)	1.925 (8)	2.175 (6)	1.913 (9)	2.175 (6)	1.89 (1)

Notes: (*a*) 1,10-Phenanthroline (Connick *et al.*, 1999); (*b*) 1,10-phenanthroline (Schutte *et al.*, 2011); (*c*) 1,10-phenanthroline (Schutte *et al.*, 2011); (*d*) 1,10-phenanthroline (Salignac *et al.*, 2003); (*e*) 4,7-diphenyl-1,10-phenanthroline (Knopf *et al.*, 2017); (*f*) 2,2′-bipyrazine (Rillema *et al.*, 2007); (*g*) 2-hydroxybenzoic acid hydrazide, (Barbazán *et al.*, 2009); (*h*) 2-(2′-pyridyl)benzothiazole (Carrington *et al.*, 2016); (*i*) 2-(2′-pyridyl)benzimidazole (Tzeng *et al.*, 2011); (*j*) acetylpyridine benzoylhydrazone (Grewe *et al.*, 2003).

points in the fingerprint plot for the complex shown in Fig. 5*d* is indicative that there are contributions from different molecules. The relative contributions for the H···H, O···H, H···F, C···H and C···C interactions are 23.2, 20.2, 16.2, 9.7 and 8.2%, respectively, which, in total, amount to 96.4%. The rest of the intermolecular interactions include O···S (3.1%), H···N (2.3%), C···S (2.4%) and C···N (1.5%), as well as other interactions with <1% contribution.

5. Database survey

A search of the Cambridge Structural Database (Version 5.39, update of August 2918; Groom *et al.*, 2016) revealed twelve *fac*-aquatricarbonyl Re^I complexes with different *N*,*N*′-bidentate ligands. A thirteenth structure, FIWQUX-2 (Schutte *et al.*, 2011), consists of two symmetry-independent complexes. The Re—N bond lengths observed in the present study (Table 2) are longer than those in most of the previously studied complexes, and close to the longer ones observed in the SEHGUK structure (Knopf *et al.*, 2017) with the 4,7-diphenyl-1,10-phenanthroline bidentate ligand. As can be seen in Table 2, the Re—N bond lengths fall in the range 2.142–2.210 Å. The corresponding range for the Re—O1*W* bond is 2.143–2.214 Å, with the value observed in the present study falling in the middle of this range. The values of the Re—C bond lengths are also given. In all cases, the Re—C bonds *trans* to water molecule are shorter than the Re—C bonds *trans* to N atoms, in accordance with the intensity of the *trans* effect of the coordinating ligands.

6. Synthesis and crystallization

A mixture of $Re(CO)_5Br$ (81 mg, 0.2 mmol) and the NNbz ligand (69 mg, 0.22 mmol) was suspended in 7 ml toluene and refluxed under an N_2 atmosphere for 4 h. The red suspension was then allowed to cool to room temperature. The red solid that formed was dissolved in acetonitrile (25 ml) and a batch of $AgPF_6$ (55 mg, 0.22 mmol) was added. The reaction mixture was refluxed for 18 h under an N_2 atmosphere. The round flask was covered with aluminium foil to avoid exposure to any ambient light. The reaction mixture was allowed to cool for 1 h to 273 K, and then the precipitate (AgBr) was filtered off through celite. The yellow–orange filtrate was evaporated to dryness under reduced pressure, and the residue was recrys-

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Re(C_{19}H_{13}N_3S)(CO)_3(H_2O)]PF_6\cdot CH_4O$
M_r	780.64
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	160
a, *b*, *c* (Å)	10.0447 (3), 10.7580 (3), 13.6263 (4)
α, β, γ (°)	74.335 (1), 76.285 (1), 68.874 (1)
V (Å^3)	1306.38 (7)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	4.88
Crystal size (mm)	0.48 × 0.26 × 0.04
Data collection	
Diffractometer	Rigaku R-AXIS SPIDER IPDS
Absorption correction	Numerical (*CrystalClear*; Rigaku, 2005)
T_{min}, T_{max}	0.496, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25647, 5694, 5416
R_{int}	0.027
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.020, 0.045, 1.06
No. of reflections	5694
No. of parameters	437
H-atom treatment	All H-atom parameters refined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.97, −0.53

Computer programs: *CrystalClear* (Rigaku, 2005), *SHELXS* (Sheldrick, 2015*a*), *SHELXL2014/6* (Sheldrick, 2015*b*), *DIAMOND* (Crystal Impact, 2012) and *publCIF* (Westrip, 2010).

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tallized from acetonitrile/water to obtain 67 mg (45% yield) of the aqua complex. Analysis calculated (%) for $C_{22}H_{15}F_6N_3O_4PReS$: C, 35.30; H, 2.02; N, 5.61; found: C: 35.43, H: 2.05, N: 5.52. IR (cm^{-1}): 2034, 1941, 1914 cm^{-1} (vibration tension of the C≡O bond), 832, 556 cm^{-1} (due to the counter-ion PF_6^-). ^1H NMR (DMSO-d_6), δ (ppm): 9.58, 9.15, 8.49, 8.45, 8.37, 8.21, 8.12, 7.98, 7.83, 7.78, 7.60, 7.52. Red–brown crystals suitable for X-ray analysis were obtained by slow evaporation from a methanol/water solution.

7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were freely refined.

Funding information

The research work was supported by the Hellenic Foundation for Research and Innovation (HFRI) and the General Secretariat for Research and Technology (GSRT) under the HFRI PhD Fellowship grant (IR, GA. No. 14500). VP would like to thank the Special Account of NCSR "Demokritos" for financial support regarding the operation of the X-ray facilities at INN through the internal program entitled ‘Structural study and characterization of crystalline materials’ (NCSR Demokritos, ELKE #10 813).

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supporting information

Acta Cryst. (2019). E**75**, 580-584 [https://doi.org/10.1107/S2056989019004298]

Crystal structure of *fac*-aqua[(*E*)-4-(benzo[*d*]thiazol-2-yl)-*N*-(pyridin-2-ylmethylidene)aniline-κ^2N,N']tricarbonylrhenium(I) hexafluoridophosphate methanol monosolvate

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Computing details

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear* (Rigaku, 2005); data reduction: *CrystalClear* (Rigaku, 2005); program(s) used to solve structure: *SHELXS* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Crystal Impact, 2012); software used to prepare material for publication: *publCIF* (Westrip, 2010).

fac-Aqua[(*E*)-4-(benzo[*d*]thiazol-2-yl)-*N*-(pyridin-2-ylmethylidene)aniline-κ^2N,N']tricarbonylrhenium(I) hexafluoridophosphate methanol monosolvate

Crystal data

$[Re(C_{19}H_{13}N_3S)(CO)_3(H_2O)]PF_6\cdot CH_4O$
$M_r = 780.64$
Triclinic, $P\overline{1}$
$a = 10.0447$ (3) Å
$b = 10.7580$ (3) Å
$c = 13.6263$ (4) Å
$\alpha = 74.335$ (1)°
$\beta = 76.285$ (1)°
$\gamma = 68.874$ (1)°
$V = 1306.38$ (7) Å^3

$Z = 2$
$F(000) = 756$
$D_x = 1.985$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 23889 reflections
$\theta = 3.2$–27.5°
$\mu = 4.88$ mm^{-1}
$T = 160$ K
Parallelepiped, red brown
0.48 × 0.26 × 0.04 mm

Data collection

Rigaku R-AXIS SPIDER IPDS diffractometer
Radiation source: fine-focus sealed tube
θ scans
Absorption correction: numerical (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.496$, $T_{max} = 1.000$
25647 measured reflections

5694 independent reflections
5416 reflections with $I > 2\sigma(I)$
$R_{int} = 0.027$
$\theta_{max} = 27.0$°, $\theta_{min} = 3.1$°
$h = -12 \rightarrow 12$
$k = -13 \rightarrow 13$
$l = -17 \rightarrow 16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.045$

$S = 1.06$
5694 reflections
437 parameters
0 restraints

Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0212P)^2 + 1.3806P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.97$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

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^2)

	x	y	z	$U_{iso}*/U_{eq}$
Re1	0.60782 (2)	0.80579 (2)	0.72803 (2)	0.02076 (4)
O1W	0.7342 (2)	0.6297 (2)	0.82936 (19)	0.0305 (4)
C1	0.7598 (3)	0.7903 (3)	0.6110 (2)	0.0278 (6)
O1	0.8494 (2)	0.7844 (2)	0.54080 (17)	0.0378 (5)
C2	0.6724 (3)	0.9386 (3)	0.7560 (2)	0.0274 (6)
O2	0.7081 (2)	1.0222 (2)	0.76923 (17)	0.0368 (5)
C3	0.4873 (3)	0.9562 (3)	0.6452 (2)	0.0270 (6)
O3	0.4169 (2)	1.0526 (2)	0.59636 (17)	0.0384 (5)
N1	0.4410 (2)	0.7968 (2)	0.86255 (17)	0.0235 (5)
N2	0.5265 (2)	0.6456 (2)	0.71983 (17)	0.0225 (4)
N3	0.8451 (2)	0.3276 (2)	0.34299 (18)	0.0255 (5)
S1	0.76531 (10)	0.12865 (8)	0.46521 (7)	0.0419 (2)
C4	0.3971 (3)	0.8740 (3)	0.9337 (2)	0.0286 (6)
C5	0.3005 (3)	0.8508 (3)	1.0224 (2)	0.0327 (6)
C6	0.2477 (4)	0.7445 (3)	1.0389 (2)	0.0362 (7)
C7	0.2894 (3)	0.6653 (3)	0.9652 (2)	0.0323 (6)
C8	0.3849 (3)	0.6940 (3)	0.8781 (2)	0.0256 (5)
C9	0.4331 (3)	0.6167 (3)	0.7970 (2)	0.0258 (6)
C10	0.5866 (3)	0.5565 (3)	0.6476 (2)	0.0230 (5)
C11	0.6169 (3)	0.4165 (3)	0.6826 (2)	0.0265 (6)
C12	0.6798 (3)	0.3310 (3)	0.6132 (2)	0.0286 (6)
C13	0.7123 (3)	0.3835 (3)	0.5087 (2)	0.0244 (5)
C14	0.6791 (3)	0.5242 (3)	0.4738 (2)	0.0249 (5)
C15	0.6175 (3)	0.6105 (3)	0.5431 (2)	0.0233 (5)
C16	0.7791 (3)	0.2926 (3)	0.4342 (2)	0.0257 (6)
C17	0.8562 (3)	0.1046 (3)	0.3433 (2)	0.0330 (7)
C18	0.8893 (4)	−0.0061 (3)	0.2976 (3)	0.0441 (8)
C19	0.9563 (4)	0.0040 (3)	0.1968 (3)	0.0415 (8)
C20	0.9923 (3)	0.1196 (3)	0.1420 (3)	0.0368 (7)
C21	0.9609 (3)	0.2297 (3)	0.1873 (2)	0.0328 (6)
C22	0.8905 (3)	0.2234 (3)	0.2887 (2)	0.0272 (6)
C1M	0.9995 (5)	0.3997 (5)	0.6743 (4)	0.0528 (10)
O1M	0.9675 (3)	0.5110 (2)	0.7203 (2)	0.0505 (7)
P1	0.72699 (9)	0.71646 (8)	1.09118 (6)	0.03265 (17)
F1	0.8471 (3)	0.6216 (3)	1.0214 (3)	0.0957 (10)

F2	0.8364 (4)	0.7745 (3)	1.1108 (2)	0.0963 (11)
F3	0.7504 (3)	0.5986 (2)	1.19014 (18)	0.0677 (7)
F4	0.6144 (3)	0.6560 (2)	1.0673 (2)	0.0683 (7)
F5	0.6990 (3)	0.8341 (2)	0.99029 (18)	0.0631 (6)
F6	0.5955 (4)	0.8096 (3)	1.1538 (3)	0.1039 (12)
H4	0.432 (3)	0.942 (3)	0.920 (3)	0.033 (9)*
H5	0.276 (4)	0.906 (4)	1.069 (3)	0.042 (10)*
H6	0.186 (4)	0.731 (3)	1.094 (3)	0.031 (8)*
H7	0.257 (4)	0.596 (4)	0.970 (3)	0.044 (10)*
H9	0.398 (3)	0.546 (3)	0.801 (2)	0.028 (8)*
H11	0.598 (3)	0.384 (3)	0.750 (2)	0.023 (7)*
H12	0.704 (3)	0.237 (3)	0.634 (3)	0.034 (8)*
H14	0.696 (3)	0.560 (3)	0.406 (3)	0.026 (8)*
H15	0.592 (3)	0.702 (3)	0.517 (2)	0.016 (7)*
H18	0.868 (4)	−0.083 (4)	0.334 (3)	0.043 (10)*
H19	0.976 (4)	−0.070 (4)	0.170 (3)	0.045 (10)*
H20	1.038 (4)	0.127 (3)	0.071 (3)	0.036 (9)*
H21	0.984 (3)	0.311 (3)	0.149 (3)	0.031 (8)*
H101	0.823 (5)	0.581 (4)	0.801 (3)	0.051 (11)*
H102	0.749 (4)	0.641 (4)	0.874 (3)	0.044 (12)*
H201	1.041 (5)	0.541 (5)	0.709 (4)	0.073 (14)*
H202	1.091 (6)	0.323 (5)	0.698 (4)	0.099 (18)*
H203	0.915 (6)	0.364 (5)	0.702 (4)	0.095 (17)*
H204	1.008 (6)	0.427 (6)	0.607 (5)	0.10 (2)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Re1	0.02758 (6)	0.01809 (5)	0.01851 (6)	−0.01022 (4)	−0.00178 (4)	−0.00422 (4)
O1W	0.0366 (12)	0.0287 (10)	0.0275 (12)	−0.0099 (9)	−0.0071 (10)	−0.0065 (9)
C1	0.0326 (14)	0.0231 (13)	0.0306 (15)	−0.0109 (11)	−0.0065 (13)	−0.0058 (11)
O1	0.0379 (12)	0.0408 (12)	0.0309 (12)	−0.0142 (10)	0.0052 (10)	−0.0079 (10)
C2	0.0333 (14)	0.0257 (13)	0.0225 (14)	−0.0106 (11)	−0.0041 (11)	−0.0020 (11)
O2	0.0531 (13)	0.0295 (10)	0.0382 (12)	−0.0228 (10)	−0.0122 (10)	−0.0056 (9)
C3	0.0338 (14)	0.0258 (13)	0.0227 (14)	−0.0134 (12)	0.0003 (11)	−0.0057 (11)
O3	0.0427 (12)	0.0308 (11)	0.0359 (12)	−0.0098 (10)	−0.0094 (10)	0.0028 (10)
N1	0.0271 (11)	0.0211 (10)	0.0220 (11)	−0.0069 (9)	−0.0025 (9)	−0.0059 (9)
N2	0.0285 (11)	0.0186 (10)	0.0227 (11)	−0.0089 (9)	−0.0038 (9)	−0.0062 (9)
N3	0.0274 (11)	0.0236 (11)	0.0270 (12)	−0.0093 (9)	−0.0015 (9)	−0.0084 (9)
S1	0.0606 (5)	0.0262 (3)	0.0392 (4)	−0.0243 (4)	0.0199 (4)	−0.0164 (3)
C4	0.0339 (15)	0.0248 (13)	0.0285 (15)	−0.0084 (12)	−0.0040 (12)	−0.0101 (11)
C5	0.0376 (16)	0.0338 (15)	0.0259 (15)	−0.0066 (13)	−0.0031 (12)	−0.0130 (13)
C6	0.0394 (17)	0.0394 (16)	0.0242 (15)	−0.0125 (14)	0.0069 (13)	−0.0080 (13)
C7	0.0364 (16)	0.0297 (14)	0.0309 (16)	−0.0155 (13)	0.0034 (13)	−0.0069 (12)
C8	0.0309 (14)	0.0218 (12)	0.0245 (14)	−0.0101 (11)	−0.0021 (11)	−0.0049 (11)
C9	0.0326 (14)	0.0231 (13)	0.0251 (14)	−0.0148 (11)	0.0003 (11)	−0.0061 (11)
C10	0.0261 (13)	0.0222 (12)	0.0238 (13)	−0.0106 (10)	−0.0014 (10)	−0.0078 (10)
C11	0.0385 (15)	0.0224 (13)	0.0186 (13)	−0.0126 (11)	−0.0013 (11)	−0.0026 (11)

C12	0.0397 (15)	0.0183 (12)	0.0286 (15)	−0.0118 (11)	−0.0028 (12)	−0.0045 (11)
C13	0.0269 (13)	0.0241 (12)	0.0251 (14)	−0.0120 (10)	0.0008 (11)	−0.0084 (11)
C14	0.0308 (14)	0.0239 (13)	0.0217 (14)	−0.0118 (11)	−0.0019 (11)	−0.0053 (11)
C15	0.0293 (13)	0.0186 (12)	0.0233 (13)	−0.0099 (10)	−0.0037 (11)	−0.0035 (10)
C16	0.0294 (13)	0.0202 (12)	0.0290 (14)	−0.0099 (10)	−0.0018 (11)	−0.0072 (11)
C17	0.0374 (15)	0.0282 (14)	0.0351 (16)	−0.0153 (12)	0.0090 (13)	−0.0152 (12)
C18	0.0501 (19)	0.0326 (16)	0.052 (2)	−0.0214 (15)	0.0175 (16)	−0.0228 (15)
C19	0.0375 (17)	0.0401 (17)	0.052 (2)	−0.0133 (14)	0.0089 (15)	−0.0310 (16)
C20	0.0329 (15)	0.0462 (18)	0.0336 (17)	−0.0127 (14)	0.0054 (13)	−0.0205 (14)
C21	0.0349 (15)	0.0338 (15)	0.0311 (16)	−0.0139 (13)	0.0009 (13)	−0.0098 (13)
C22	0.0255 (13)	0.0274 (13)	0.0316 (15)	−0.0104 (11)	−0.0004 (11)	−0.0112 (12)
C1M	0.049 (2)	0.058 (2)	0.066 (3)	−0.0270 (19)	−0.001 (2)	−0.029 (2)
O1M	0.0334 (12)	0.0402 (13)	0.081 (2)	−0.0137 (10)	0.0051 (12)	−0.0265 (13)
P1	0.0454 (4)	0.0270 (4)	0.0253 (4)	−0.0160 (3)	−0.0040 (3)	−0.0003 (3)
F1	0.088 (2)	0.0651 (16)	0.104 (2)	−0.0127 (15)	0.0385 (17)	−0.0299 (16)
F2	0.147 (3)	0.108 (2)	0.0777 (19)	−0.102 (2)	−0.0657 (19)	0.0366 (17)
F3	0.0950 (18)	0.0641 (14)	0.0560 (14)	−0.0505 (14)	−0.0404 (13)	0.0284 (12)
F4	0.0874 (17)	0.0592 (14)	0.0723 (16)	−0.0459 (13)	−0.0405 (14)	0.0199 (12)
F5	0.0817 (16)	0.0568 (13)	0.0504 (13)	−0.0385 (12)	−0.0226 (12)	0.0233 (11)
F6	0.130 (3)	0.0520 (15)	0.096 (2)	−0.0228 (16)	0.052 (2)	−0.0301 (15)

Geometric parameters (Å, º)

Re1—C3	1.899 (3)	C11—C12	1.380 (4)
Re1—C2	1.920 (3)	C11—H11	0.89 (3)
Re1—C1	1.925 (3)	C12—C13	1.389 (4)
Re1—N1	2.177 (2)	C12—H12	0.93 (3)
Re1—O1W	2.189 (2)	C13—C14	1.397 (4)
Re1—N2	2.194 (2)	C13—C16	1.475 (4)
O1W—H101	0.91 (4)	C14—C15	1.386 (4)
O1W—H102	0.72 (4)	C14—H14	0.90 (3)
C1—O1	1.146 (4)	C15—H15	0.92 (3)
C2—O2	1.150 (3)	C17—C18	1.390 (4)
C3—O3	1.158 (3)	C17—C22	1.410 (4)
N1—C4	1.339 (3)	C18—C19	1.373 (5)
N1—C8	1.361 (3)	C18—H18	0.92 (4)
N2—C9	1.284 (3)	C19—C20	1.389 (5)
N2—C10	1.436 (3)	C19—H19	0.90 (4)
N3—C16	1.289 (4)	C20—C21	1.384 (4)
N3—C22	1.390 (3)	C20—H20	0.96 (3)
S1—C17	1.733 (3)	C21—C22	1.390 (4)
S1—C16	1.748 (3)	C21—H21	0.96 (3)
C4—C5	1.385 (4)	C1M—O1M	1.401 (4)
C4—H4	0.89 (3)	C1M—H202	1.04 (6)
C5—C6	1.372 (4)	C1M—H203	1.01 (6)
C5—H5	0.91 (4)	C1M—H204	0.87 (6)
C6—C7	1.385 (4)	O1M—H201	0.88 (5)
C6—H6	0.87 (3)	P1—F2	1.547 (2)

C7—C8	1.378 (4)	P1—F6	1.565 (3)
C7—H7	0.89 (4)	P1—F1	1.579 (3)
C8—C9	1.450 (4)	P1—F3	1.579 (2)
C9—H9	0.94 (3)	P1—F5	1.600 (2)
C10—C15	1.392 (4)	P1—F4	1.621 (2)
C10—C11	1.393 (4)		

C3—Re1—C2	85.26 (12)	C11—C12—H12	122 (2)
C3—Re1—C1	89.26 (12)	C13—C12—H12	118 (2)
C2—Re1—C1	87.63 (12)	C12—C13—C14	119.5 (2)
C3—Re1—N1	95.27 (10)	C12—C13—C16	120.8 (2)
C2—Re1—N1	98.04 (10)	C14—C13—C16	119.7 (2)
C1—Re1—N1	173.00 (9)	C15—C14—C13	120.2 (3)
C3—Re1—O1W	176.33 (10)	C15—C14—H14	119.4 (19)
C2—Re1—O1W	96.59 (10)	C13—C14—H14	120.3 (19)
C1—Re1—O1W	93.97 (10)	C14—C15—C10	119.7 (2)
N1—Re1—O1W	81.35 (8)	C14—C15—H15	118.1 (18)
C3—Re1—N2	99.29 (10)	C10—C15—H15	122.0 (18)
C2—Re1—N2	171.90 (10)	N3—C16—C13	124.0 (2)
C1—Re1—N2	99.07 (10)	N3—C16—S1	115.7 (2)
N1—Re1—N2	74.96 (8)	C13—C16—S1	120.2 (2)
O1W—Re1—N2	78.50 (8)	C18—C17—C22	121.5 (3)
Re1—O1W—H101	118 (2)	C18—C17—S1	129.6 (2)
Re1—O1W—H102	117 (3)	C22—C17—S1	108.8 (2)
H101—O1W—H102	102 (4)	C19—C18—C17	117.7 (3)
O1—C1—Re1	178.4 (2)	C19—C18—H18	122 (2)
O2—C2—Re1	177.0 (2)	C17—C18—H18	121 (2)
O3—C3—Re1	176.2 (2)	C18—C19—C20	121.6 (3)
C4—N1—C8	117.9 (2)	C18—C19—H19	115 (2)
C4—N1—Re1	127.09 (19)	C20—C19—H19	123 (2)
C8—N1—Re1	114.86 (17)	C21—C20—C19	120.9 (3)
C9—N2—C10	118.0 (2)	C21—C20—H20	117 (2)
C9—N2—Re1	115.25 (18)	C19—C20—H20	122 (2)
C10—N2—Re1	125.69 (16)	C20—C21—C22	118.7 (3)
C16—N3—C22	111.1 (2)	C20—C21—H21	121.0 (19)
C17—S1—C16	89.41 (13)	C22—C21—H21	120.2 (19)
N1—C4—C5	122.5 (3)	N3—C22—C21	125.6 (3)
N1—C4—H4	116 (2)	N3—C22—C17	114.9 (2)
C5—C4—H4	122 (2)	C21—C22—C17	119.4 (3)
C6—C5—C4	119.2 (3)	O1M—C1M—H202	111 (3)
C6—C5—H5	122 (2)	O1M—C1M—H203	105 (3)
C4—C5—H5	119 (2)	H202—C1M—H203	108 (4)
C5—C6—C7	119.1 (3)	O1M—C1M—H204	109 (4)
C5—C6—H6	119 (2)	H202—C1M—H204	113 (5)
C7—C6—H6	122 (2)	H203—C1M—H204	111 (5)
C8—C7—C6	119.0 (3)	C1M—O1M—H201	112 (3)
C8—C7—H7	117 (2)	F2—P1—F6	93.4 (2)
C6—C7—H7	124 (2)	F2—P1—F1	92.4 (2)

N1—C8—C7	122.2 (3)	F6—P1—F1	173.6 (2)
N1—C8—C9	115.3 (2)	F2—P1—F3	92.81 (13)
C7—C8—C9	122.4 (2)	F6—P1—F3	91.03 (17)
N2—C9—C8	119.2 (2)	F1—P1—F3	91.27 (16)
N2—C9—H9	120.4 (19)	F2—P1—F5	89.19 (13)
C8—C9—H9	120.4 (19)	F6—P1—F5	88.71 (16)
C15—C10—C11	120.3 (2)	F1—P1—F5	88.78 (16)
C15—C10—N2	119.7 (2)	F3—P1—F5	177.99 (13)
C11—C10—N2	120.0 (2)	F2—P1—F4	178.45 (17)
C12—C11—C10	119.7 (3)	F6—P1—F4	87.72 (18)
C12—C11—H11	121.4 (19)	F1—P1—F4	86.42 (17)
C10—C11—H11	118.8 (19)	F3—P1—F4	88.27 (12)
C11—C12—C13	120.6 (2)	F5—P1—F4	89.73 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5···O2^{i}	0.91 (4)	2.59 (4)	3.439 (4)	156 (3)
C9—H9···F3^{ii}	0.94 (3)	2.47 (3)	3.390 (3)	166 (2)
O1*W*—H101···O1*M*	0.91 (4)	1.67 (4)	2.558 (3)	165 (4)
O1*W*—H102···F1	0.72 (4)	2.36 (4)	3.059 (5)	164 (4)
O1*M*—H201···N3^{iii}	0.88 (5)	2.01 (5)	2.842 (3)	158 (4)

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+2; (ii) −*x*+1, −*y*+1, −*z*+2; (iii) −*x*+2, −*y*+1, −*z*+1.