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## An Unexpected Rhenium(IV)–Rhenium(VII) Salt: [Co(NH<sub>3</sub>)<sub>6</sub>]<sub>3</sub>[ReVIIO<sub>4</sub>][ReIVF<sub>6</sub>]·46H<sub>2</sub>O

James Louis\_Jean

University of Nevada, Las Vegas, james.louis-jean@unlv.edu

Samudee Mariappan Balasekaran

University of Nevada, Las Vegas, samundeeswari.mariappanbalasekaran@unlv.edu

Adelheid Hagenbach

University of Berlin

Frederic Poineau

University of Nevada, Las Vegas, frederic.poineau@unlv.edu

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# An unexpected rhenium(IV)–rhenium(VII) salt: [Co(NH<sub>3</sub>)<sub>6</sub>]<sub>3</sub>[Re<sup>VII</sup>O<sub>4</sub>][Re<sup>IV</sup>F<sub>6</sub>]<sub>4</sub>·6H<sub>2</sub>O

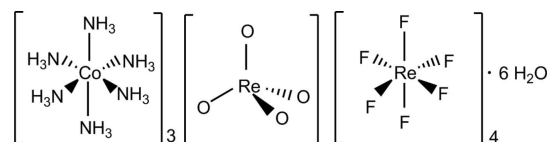
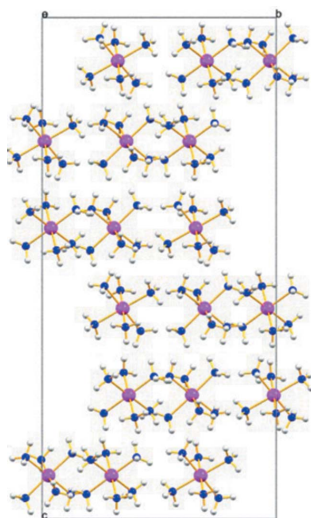
James Louis–Jean,<sup>a\*</sup> Samundeeswari Mariappan Balasekaran,<sup>a</sup> Adelheid  
Hagenbach<sup>b</sup> and Frederic Poineau<sup>a</sup><sup>a</sup>Department of Chemistry and Biochemistry, University of Nevada Las Vegas, 4505 South Maryland Parkway, Las Vegas,  
Nevada, 89154, USA, and <sup>b</sup>Department of Chemistry and Biochemistry, Freie University Berlin, Berlin 14195, Germany.

\*Correspondence e-mail: louisjea@unlv.nevada.edu

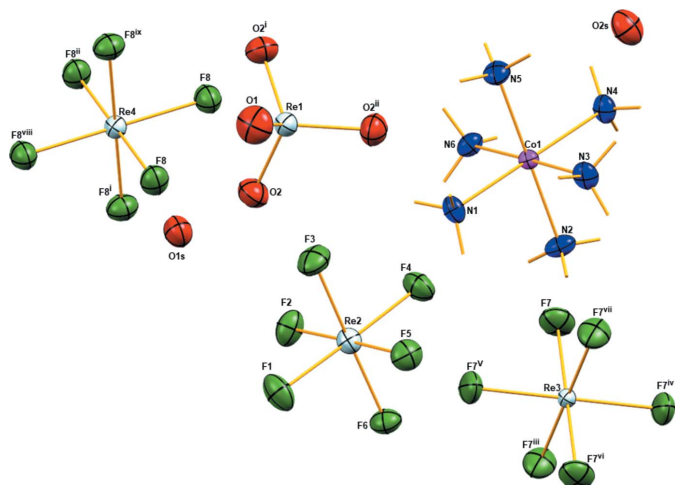
The title hydrated salt, tris[hexaamminecobalt(III)] tetraoxidorhenate(VII) tetrakis[hexafluoridorhenate(IV)] hexahydrate, arose unexpectedly due to possible contamination of the K<sub>2</sub>ReF<sub>6</sub> starting material with KReO<sub>4</sub>. It consists of octahedral [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> cation (Co1 site symmetry 1), tetrahedral [Re<sup>VII</sup>O<sub>4</sub>]<sup>−</sup> anions (Re site symmetry 1) and octahedral [Re<sup>IV</sup>F<sub>6</sub>]<sup>2−</sup> anions (Re site symmetries 1 and  $\bar{3}$ ). The [ReF<sub>6</sub>]<sup>2−</sup> octahedral anions (mean Re–F = 1.834 Å), [Co(NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> octahedral cations (mean Co–N = 1.962 Å), and the [ReO<sub>4</sub>]<sup>−</sup> tetrahedral anion (mean Re–O = 1.719 Å) are slightly distorted. A network of N–H...F hydrogen bonds consolidates the structure. The crystal studied was refined as a two-component twin.

## 1. Chemical context

The chemistry of Re<sup>VII</sup> is dominated by the tetrahedral perrhenate anion, [ReO<sub>4</sub>]<sup>−</sup> (Latimer, 1952; Abram, 2003) while Re<sup>IV</sup> is typically found in salts containing octahedral [ReX<sub>6</sub>]<sup>2−</sup> (X = F, Cl, Br, I) anions (Berthold & Jakobson, 1964; Jorgensen & Schwochau, 1965; Grundy & Brown, 1970; Louis-Jean *et al.*, 2018). The salts of [ReX<sub>6</sub>]<sup>2−</sup> (X = Cl, Br, I) can be prepared in high yield by the reduction of a perrhenate starting material in the corresponding concentrated HX acid (Briscoe *et al.*, 1931; Watt *et al.*, 1963). However, salts of [ReF<sub>6</sub>]<sup>2−</sup> are typically prepared from the solid-state melting reaction of [ReX<sub>6</sub>]<sup>2−</sup> (X = Cl, Br, I) with AHF<sub>2</sub> (A = NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>) followed by an aqueous work-up (Ruff & Kwasnik, 1934; Louis-Jean *et al.*, 2018). Such a procedure is found to be challenging. Nonetheless, an improved procedure for the preparation of A<sub>2</sub>[ReF<sub>6</sub>] (A = K, Rb, Cs) salts as well as their X-ray single-crystal structures was recently reported (Louis-Jean *et al.*, 2018).



In the process of exploring the coordination chemistry of hexafluororhenate(IV) compounds, the title compound (**I**), an unexpected mixed-valence rhenium(IV)–rhenium(VII) salt arose in an effort to prepare [Co(NH<sub>3</sub>)<sub>6</sub>]<sub>2</sub>[ReF<sub>6</sub>]<sub>3</sub> by metathesis from K<sub>2</sub>[ReF<sub>6</sub>] and Co(NH<sub>3</sub>)<sub>6</sub>Cl<sub>3</sub> in water (353 K). Yellow–orange needle-like crystals of (**I**) were obtained within two hours by slow evaporation in water at room temperature.


**Figure 1**

The molecular structure of **(I)** showing displacement ellipsoids drawn at the 50% probability level for all non-H atoms. Symmetry codes: (i)  $1 - x + y, 1 - x, z$ ; (ii)  $1 - y, x - y, z$ ; (iii)  $\frac{1}{3} + y, \frac{2}{3} - x + y, \frac{5}{3} - z$ ; (iv)  $\frac{1}{3} + x - y, -\frac{1}{3} + x, \frac{2}{3} - z$ ; (v)  $\frac{4}{3} - x, \frac{2}{3} - y, \frac{5}{3} - z$ ; (vi)  $\frac{2}{3} + x - y, \frac{1}{3} + x, \frac{4}{3} - z$ ; (vii)  $-\frac{1}{3} + y, \frac{1}{3} - x + y, \frac{4}{3} - z$ ; (viii)  $\frac{2}{3} - x, \frac{4}{3} - y, \frac{4}{3} - z$ ; (ix)  $-x + y, 1 - x, z$ ; (x)  $1 - y, 1 + x - y, z$ .

The crystals of **(I)** are air stable over short periods, but decompose to a black material after six months of storage at ambient temperature.

## 2. Structural commentary

The structure of **(I)** (Fig. 1) is built up from a  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cation, three distinct  $[\text{ReF}_6]^{2-}$  anions, one  $[\text{ReO}_4]^-$  anion, and two water molecules of crystallization: these components are held together by electrostatic forces and hydrogen bonding. Site symmetries for the metal atoms are Co1: 1 (Wyckoff position 18f), Re1: 3 (Wyckoff position 6c), Re2: 1 (Wyckoff

position 18f), Re3:  $\bar{3}$  (Wyckoff position 3a), and Re4:  $\bar{3}$  (Wyckoff position 3b).

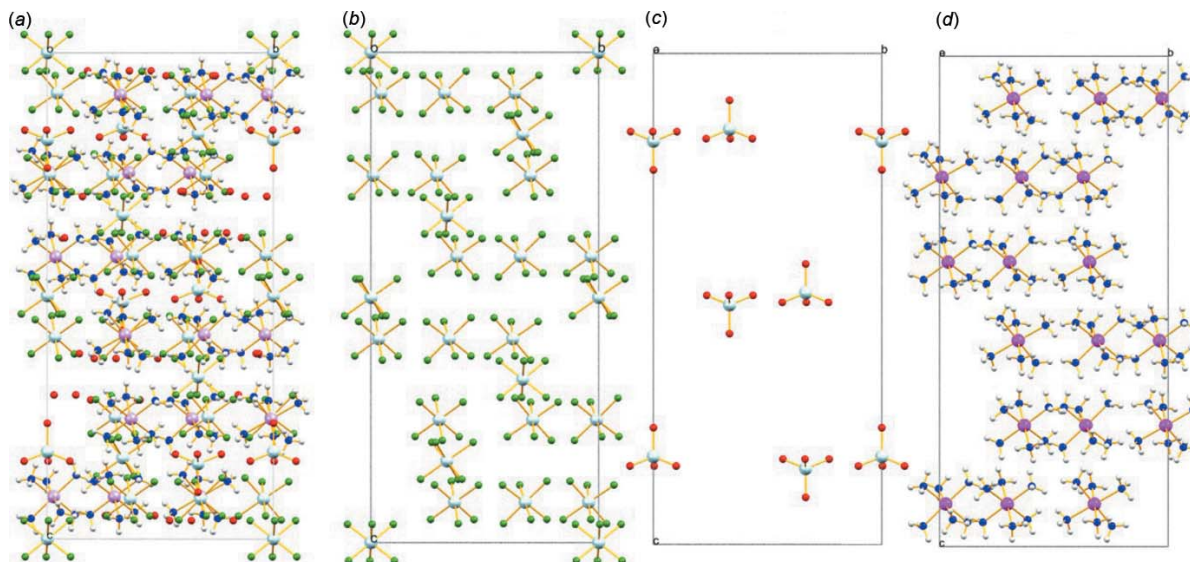
The octahedral  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cation in **(I)** is slightly distorted; the average Co–N bond length of 1.962 Å is in agreement with the average Co–N bond lengths of 1.963 Å in  $[\text{Co}(\text{NH}_3)_6](\text{ReO}_4) \cdot 2\text{H}_2\text{O}$  (Baidina *et al.*, 2012) and 1.966 Å in  $[\text{Co}(\text{NH}_3)_6](\text{TcO}_4)_3$  (Poineau *et al.*, 2017). In **(I)**, the shortest Co···Co and N···N separations between nearby  $[\text{Co}(\text{NH}_3)_6]^{3+}$  cations are 7.035 (1) and 4.473 (1) Å, respectively.

In the tetrahedral  $[\text{ReO}_4]^-$  anion in **(I)**, the average Re–O bond length (1.719 Å) is in agreement with the average Re–O bond length of 1.720 Å in  $[\text{Co}(\text{NH}_3)_6](\text{ReO}_4) \cdot 2\text{H}_2\text{O}$  (Baidina *et al.*, 2012). In **(I)** the values of three Re–O bond lengths,  $[\text{Re1}-\text{O2}^i, \text{Re}-\text{O2}$  and  $\text{Re}-\text{O2}^{ii} = 1.715$  (8) Å; symmetry codes: (i)  $1 - x + y, 1 - x, z$ ; (ii)  $1 - y, x - y, z$ ] are slightly shorter than the fourth one  $[\text{Re}-\text{O1} = 1.748$  (14) Å]. In **(I)**, all O–Re–O bond angles in the  $[\text{ReO}_4]^-$  anion are 109.5 (3)°. However, in  $[\text{Co}(\text{NH}_3)_6](\text{ReO}_4) \cdot 2\text{H}_2\text{O}$ , the  $[\text{ReO}_4]^-$  anion is slightly distorted by up to 2.7° (Baidina *et al.*, 2012).

The  $[\text{ReF}_6]^{2-}$  anions are slightly distorted, with Re–F bond lengths varying from 1.916 (6) Å to 1.929 (6) Å. All the Re–F bond lengths in the Re3- and Re4-centred anions are of equal distances of 1.952 (6) and 1.950 (6) Å, respectively, by symmetry. Overall, the average Re–F bond length (1.834 Å) in **(I)** is notably shorter than the average Re–F bond length (1.951 Å) in  $A_2[\text{ReF}_6]$  ( $A = \text{K}, \text{Rb}, \text{Cs}$ ) salts previously studied (Louis-Jean *et al.*, 2018).

## 3. Supramolecular features

A perspective view of the unit-cell plots for **(I)** and its component ions ( $[\text{ReF}_6]^{2-}$ ,  $[\text{ReO}_4]^-$ , and  $[\text{Co}(\text{NH}_3)_6]^{3+}$ ) are shown in Fig. 2. In the supramolecular structure of the title


**Figure 2**

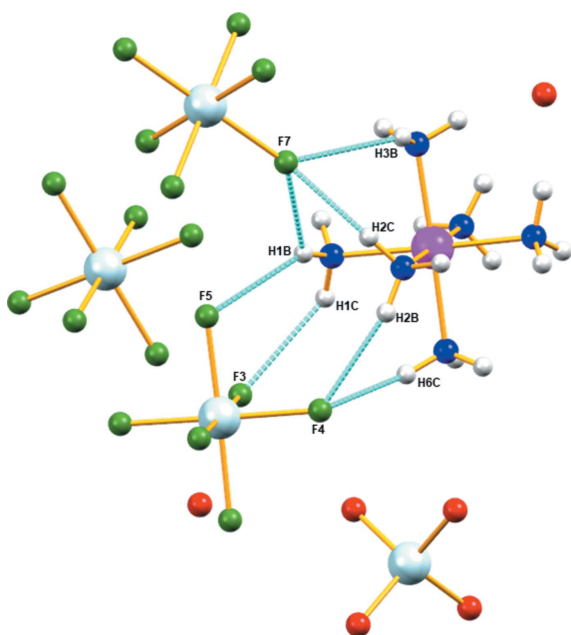
Unit-cell plots showing only (a) the complete structure of **(I)**, (b) the  $[\text{ReF}_6]^{2-}$  octahedra, (c) the  $[\text{ReO}_4]^-$  tetrahedra and (d) the  $[\text{Co}(\text{NH}_3)_6]^{3+}$  octahedra viewed along the crystallographic  $b$  axis. Color of atoms: Re aqua blue, F green, Co purple, N blue, O red, H gray.

**Table 1**  
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>
N1—H1A···F1 <sup>i</sup>	0.89	2.34	3.085 (11)	141
N1—H1A···F5 <sup>i</sup>	0.89	2.29	3.078 (10)	148
N1—H1B···F5	0.89	2.32	3.037 (10)	138
N1—H1B···F7	0.89	2.42	3.098 (11)	133
N1—H1C···F3	0.89	2.40	3.144 (10)	141
N1—H1C···O1S <sup>ii</sup>	0.89	2.35	3.084 (12)	140
N2—H2A···F2 <sup>iii</sup>	0.89	2.46	3.243 (10)	148
N2—H2A···O2 <sup>iii</sup>	0.89	2.54	3.089 (12)	121
N2—H2B···F4	0.89	2.31	3.137 (12)	155
N2—H2B···F4 <sup>iii</sup>	0.89	2.58	3.161 (10)	124
N2—H2C···F7	0.89	2.08	2.928 (10)	158
N3—H3A···F6 <sup>iv</sup>	0.89	2.57	3.054 (10)	115
N3—H3A···O2S	0.89	2.26	3.027 (12)	145
N3—H3B···F5 <sup>iv</sup>	0.89	2.52	3.132 (10)	127
N3—H3B···F7	0.89	2.32	2.911 (11)	123
N3—H3C···F5 <sup>i</sup>	0.89	2.24	3.112 (10)	166
N4—H4A···F2 <sup>iii</sup>	0.89	2.16	3.038 (10)	170
N4—H4A···F6 <sup>iii</sup>	0.89	2.57	3.126 (10)	121
N4—H4B···F6 <sup>iv</sup>	0.89	2.19	2.969 (10)	146
N4—H4C···F8 <sup>v</sup>	0.89	2.21	3.019 (11)	150
N5—H5A···O2S	0.89	2.08	2.936 (12)	162
N5—H5B···F1 <sup>i</sup>	0.89	2.20	3.057 (11)	162
N5—H5C···F1 <sup>ii</sup>	0.89	2.49	3.019 (11)	119
N5—H5C···F2 <sup>ii</sup>	0.89	2.43	3.261 (11)	157
N6—H6A···F4 <sup>iii</sup>	0.89	2.55	3.110 (10)	122
N6—H6A···F6 <sup>iii</sup>	0.89	2.16	3.037 (10)	168
N6—H6B···F2 <sup>ii</sup>	0.89	2.16	2.968 (10)	151
N6—H6B···O1S <sup>ii</sup>	0.89	2.67	3.227 (11)	122
N6—H6C···F4	0.89	2.14	2.982 (10)	159

Symmetry codes: (i)  $y - \frac{1}{3}, -x + y + \frac{1}{3}, -z + \frac{4}{3}$ ; (ii)  $-y + 1, x - y, z$ ; (iii)  $-x + 1, -y + 1, -z + 1$ ; (iv)  $-x + y, -x + 1, z$ ; (v)  $-x + \frac{2}{3}, -y + \frac{1}{3}, -z + \frac{4}{3}$ .

compound, the ammine ligands of the cations form numerous N—H···F and N—H···O hydrogen bonds with the fluorine atoms of [ReF<sub>6</sub>]<sup>2-</sup> anions and the water molecules (Table 1, Fig. 3).



**Figure 3**  
Detail of the hydrogen bonding (blue dotted lines) in **(I)**. Atom colors as in Fig. 2.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	[Co(NH <sub>3</sub> ) <sub>6</sub> ] <sub>3</sub> [ReO <sub>4</sub> ][ReF <sub>6</sub> ] <sub>4</sub> ·6H <sub>2</sub> O
<i>M<sub>r</sub></i>	2030.40
Crystal system, space group	Trigonal, <i>R</i> $\bar{3}$
Temperature (K)	293
<i>a</i> , <i>c</i> (Å)	15.982 (3), 29.740 (5)
<i>V</i> (Å <sup>3</sup> )	6579 (2)
<i>Z</i>	6
Radiation type	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	15.00
Crystal size (mm)	0.63 × 0.08 × 0.07
Data collection	
Diffractometer	Bruker D8 QUEST
Absorption correction	Numerical (Krause <i>et al.</i> , 2015)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.02, 0.43
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	45169, 5223, 4885
<i>R<sub>int</sub></i>	0.082
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.635
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.039, 0.114, 1.08
No. of reflections	5223
No. of parameters	189
H-atom treatment	H-atom parameters constrained
Δρ <sub>max</sub> , Δρ <sub>min</sub> (e Å <sup>-3</sup> )	2.36, -4.16

Computer programs: *APEX3* and *SAINT* (Bruker, 2015), *SHELXT* (Sheldrick, 2015a), *SHELXL2014* (Sheldrick, 2015b) and *shelXle* (Hübschle *et al.*, 2011).

## 4. Database survey

To the best of our knowledge, **(I)** is the only reported hexahalogenorhenate–perrhenate structure containing both rhenium(IV) and rhenium(VII). It is noted that K<sub>2</sub>[ReF<sub>6</sub>] used for the preparation of **(I)** was not characterized before use and the presence of perrhenate in **(I)** may be due to the presence of K[ReO<sub>4</sub>] in the starting material. Efforts to isolate the technetium (Tc-99) derivative compound, [Co(NH<sub>3</sub>)<sub>6</sub>]<sub>3</sub>[(Tc<sup>(vii)</sup>O<sub>4</sub>)(Tc<sup>(iv)</sup>F<sub>6</sub>)<sub>4</sub>] are in progress.

## 5. Synthesis and crystallization

All chemicals were obtained commercially from Sigma Aldrich® and used without any further purification. The starting material, K<sub>2</sub>[ReF<sub>6</sub>], was prepared following the method described in our previous publication (Louis-Jean *et al.*, 2018).

K<sub>2</sub>[ReF<sub>6</sub>] (114 mg, 0.3 mmol) was dissolved in 2 ml of hot water (353 K), and [Co(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> (53.5 mg, 0.2 mmol) dissolved in 1 ml of H<sub>2</sub>O was added. The solution was allowed to evaporate slowly at room temperature and yellow-orange needle-like crystals of **(I)** were obtained within two hours. The compound was washed with H<sub>2</sub>O (3 × 1 ml), followed by isopropanol (3 × 1 ml) and then diethyl ether (3 × 1 ml). Single crystals of **(I)** were grown in H<sub>2</sub>O by slow evaporation at room temperature. Yield: *ca* 91%. The presence of perrhenate in **(I)** is probably due to the presence of K[ReO<sub>4</sub>] in the starting material (*i.e.* K<sub>2</sub>ReF<sub>6</sub>).

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The H atoms of the co-crystallized water molecules could not be located in the present experiment.

## Acknowledgements

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## supporting information

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## An unexpected rhenium(IV)–rhenium(VII) salt: $[\text{Co}(\text{NH}_3)_6]_3[\text{Re}^{\text{VII}}\text{O}_4][\text{Re}^{\text{IV}}\text{F}_6]_4 \cdot 6\text{H}_2\text{O}$

James Louis–Jean, Samundeeswari Mariappan Balasekaran, Adelheid Hagenbach and Frederic Poineau

### Computing details

Data collection: *APEX3* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *shelXle* (Hübschle *et al.*, 2011); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015b).

### Tris[hexaamminecobalt(III)] tetraoxidorhenate(VII) tetrakis[hexafluoridorhenate(IV)] hexahydrate

#### Crystal data

$[\text{Co}(\text{NH}_3)_6]_3[\text{ReO}_4][\text{ReF}_6]_4 \cdot 6\text{H}_2\text{O}$   
 $M_r = 2030.40$   
 Trigonal,  $R\bar{3}$   
 $a = 15.982(3) \text{ \AA}$   
 $c = 29.740(5) \text{ \AA}$   
 $V = 6579(2) \text{ \AA}^3$   
 $Z = 6$   
 $F(000) = 5592$

$D_x = 3.075 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$   
 Cell parameters from 618 reflections  
 $\theta = 3.2\text{--}32.0^\circ$   
 $\mu = 15.00 \text{ mm}^{-1}$   
 $T = 293 \text{ K}$   
 Rectangular box, translucent orange  
 $0.63 \times 0.08 \times 0.07 \text{ mm}$

#### Data collection

Bruker D8 QUEST  
 diffractometer  
 Radiation source: sealed tube, Siemens  
 KFFMo2K-90  
 Curved graphite monochromator  
 Detector resolution:  $8.3333 \text{ pixels mm}^{-1}$   
 ' $\varphi$  and  $\omega$  scans'  
 Absorption correction: numerical  
 (Krause *et al.*, 2015)

$T_{\min} = 0.02$ ,  $T_{\max} = 0.43$   
 45169 measured reflections  
 5223 independent reflections  
 4885 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.082$   
 $\theta_{\max} = 26.8^\circ$ ,  $\theta_{\min} = 1.6^\circ$   
 $h = -20 \rightarrow 20$   
 $k = -20 \rightarrow 20$   
 $l = -37 \rightarrow 37$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.039$   
 $wR(F^2) = 0.114$   
 $S = 1.08$   
 5223 reflections  
 189 parameters  
 0 restraints

Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0476P)^2 + 166.9724P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.002$   
 $\Delta\rho_{\max} = 2.36 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -4.16 \text{ e \AA}^{-3}$

*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.

**Refinement.** Refined as a 2-component twin.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Co1	0.30664 (8)	0.34382 (8)	0.58013 (3)	0.0133 (2)
N1	0.4055 (5)	0.4205 (6)	0.6252 (2)	0.0215 (15)
H1A	0.3824	0.3987	0.6526	0.032*
H1B	0.4211	0.4822	0.623	0.032*
H1C	0.4577	0.4154	0.6205	0.032*
N2	0.3377 (7)	0.4637 (6)	0.5488 (3)	0.0257 (17)
H2A	0.2965	0.4506	0.5262	0.038*
H2B	0.3977	0.4909	0.538	0.038*
H2C	0.3333	0.5041	0.5679	0.038*
N3	0.2114 (6)	0.3556 (6)	0.6173 (3)	0.0244 (16)
H3A	0.1533	0.3039	0.6133	0.037*
H3B	0.2098	0.4085	0.6094	0.037*
H3C	0.228	0.3597	0.6461	0.037*
N4	0.2051 (6)	0.2661 (6)	0.5359 (3)	0.0236 (16)
H4A	0.22	0.2963	0.5095	0.035*
H4B	0.1488	0.2582	0.5454	0.035*
H4C	0.2008	0.2086	0.5329	0.035*
N5	0.2754 (6)	0.2239 (6)	0.6122 (3)	0.0255 (17)
H5A	0.2133	0.1932	0.62	0.038*
H5B	0.3118	0.2381	0.6367	0.038*
H5C	0.2869	0.1861	0.5943	0.038*
N6	0.4042 (6)	0.3341 (6)	0.5441 (2)	0.0220 (15)
H6A	0.3851	0.3229	0.5155	0.033*
H6B	0.4115	0.2859	0.5544	0.033*
H6C	0.4602	0.3893	0.546	0.033*
Re2	0.65656 (3)	0.62285 (3)	0.58421 (2)	0.02226 (14)
F1	0.7514 (5)	0.7013 (5)	0.6281 (2)	0.0413 (16)
F2	0.7555 (5)	0.6161 (5)	0.5496 (2)	0.0356 (14)
F3	0.6309 (5)	0.5116 (5)	0.6198 (2)	0.0411 (16)
F4	0.5603 (5)	0.5407 (5)	0.5415 (2)	0.0368 (14)
F5	0.5608 (5)	0.6319 (5)	0.6196 (2)	0.0337 (14)
F6	0.6801 (5)	0.7340 (4)	0.54917 (19)	0.0306 (12)
Re1	0.6667	0.3333	0.51213 (2)	0.02289 (17)
O1	0.6667	0.3333	0.5709 (5)	0.048 (4)
O2	0.7663 (6)	0.4359 (6)	0.4929 (3)	0.0384 (17)
Re4	0.6667	0.3333	0.8333	0.01831 (19)
F8	0.5515 (4)	0.2843 (5)	0.7957 (2)	0.0336 (13)
Re3	0.3333	0.6667	0.6667	0.01401 (18)

F7	0.3284 (5)	0.5638 (5)	0.6295 (2)	0.0396 (15)
O1S	0.7924 (6)	0.4886 (6)	0.6292 (3)	0.0379 (18)
O2S	0.0654 (6)	0.1416 (6)	0.6190 (3)	0.0417 (19)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Co1	0.0161 (5)	0.0146 (5)	0.0097 (5)	0.0079 (4)	0.0003 (4)	-0.0008 (4)
N1	0.019 (4)	0.028 (4)	0.014 (3)	0.009 (3)	-0.001 (3)	-0.003 (3)
N2	0.040 (5)	0.022 (4)	0.019 (4)	0.019 (4)	0.003 (4)	0.002 (3)
N3	0.027 (4)	0.030 (4)	0.018 (4)	0.015 (4)	-0.003 (3)	-0.009 (3)
N4	0.025 (4)	0.032 (4)	0.016 (4)	0.015 (3)	-0.005 (3)	-0.006 (3)
N5	0.029 (4)	0.024 (4)	0.022 (4)	0.013 (3)	0.002 (3)	0.006 (3)
N6	0.029 (4)	0.025 (4)	0.019 (4)	0.018 (3)	0.003 (3)	0.000 (3)
Re2	0.0227 (2)	0.0252 (2)	0.0173 (2)	0.01086 (15)	0.00121 (13)	0.00071 (13)
F1	0.033 (3)	0.051 (4)	0.026 (3)	0.010 (3)	-0.006 (3)	-0.006 (3)
F2	0.039 (3)	0.053 (4)	0.027 (3)	0.032 (3)	0.007 (3)	0.004 (3)
F3	0.044 (4)	0.038 (4)	0.045 (4)	0.023 (3)	0.009 (3)	0.018 (3)
F4	0.035 (3)	0.033 (3)	0.031 (3)	0.009 (3)	-0.007 (3)	-0.005 (3)
F5	0.035 (3)	0.038 (3)	0.030 (3)	0.019 (3)	0.010 (3)	0.004 (3)
F6	0.039 (3)	0.026 (3)	0.027 (3)	0.016 (3)	0.003 (3)	0.005 (2)
Re1	0.0219 (2)	0.0219 (2)	0.0248 (3)	0.01097 (11)	0	0
O1	0.058 (6)	0.058 (6)	0.028 (7)	0.029 (3)	0	0
O2	0.030 (4)	0.033 (4)	0.043 (4)	0.010 (3)	0.001 (3)	0.001 (3)
Re4	0.0199 (3)	0.0199 (3)	0.0151 (4)	0.00997 (13)	0	0
F8	0.030 (3)	0.033 (3)	0.034 (3)	0.013 (3)	-0.005 (3)	0.001 (3)
Re3	0.0135 (2)	0.0135 (2)	0.0151 (4)	0.00674 (12)	0	0
F7	0.042 (4)	0.034 (3)	0.043 (4)	0.019 (3)	0.003 (3)	-0.015 (3)
O1S	0.033 (4)	0.040 (4)	0.039 (4)	0.017 (4)	-0.006 (3)	-0.003 (3)
O2S	0.032 (4)	0.048 (5)	0.038 (4)	0.015 (4)	0.005 (3)	-0.004 (4)

*Geometric parameters (Å, °)*

Co1—N2	1.958 (8)	N6—H6C	0.89
Co1—N6	1.960 (7)	Re2—F1	1.916 (6)
Co1—N1	1.965 (7)	Re2—F4	1.918 (6)
Co1—N3	1.965 (8)	Re2—F5	1.922 (6)
Co1—N5	1.968 (8)	Re2—F6	1.928 (6)
Co1—N4	1.972 (8)	Re2—F3	1.929 (6)
N1—H1A	0.89	Re2—F2	1.934 (6)
N1—H1B	0.89	Re1—O2 <sup>i</sup>	1.715 (8)
N1—H1C	0.89	Re1—O2	1.715 (8)
N2—H2A	0.89	Re1—O2 <sup>ii</sup>	1.715 (8)
N2—H2B	0.89	Re1—O1	1.748 (14)
N2—H2C	0.89	Re4—F8 <sup>iii</sup>	1.952 (6)
N3—H3A	0.89	Re4—F8 <sup>iv</sup>	1.952 (6)
N3—H3B	0.89	Re4—F8 <sup>ii</sup>	1.952 (6)
N3—H3C	0.89	Re4—F8 <sup>v</sup>	1.952 (6)



N4—H4A	0.89	Re4—F8	1.952 (6)
N4—H4B	0.89	Re4—F8 <sup>i</sup>	1.952 (6)
N4—H4C	0.89	Re3—F7 <sup>vi</sup>	1.950 (6)
N5—H5A	0.89	Re3—F7 <sup>vii</sup>	1.950 (6)
N5—H5B	0.89	Re3—F7	1.950 (6)
N5—H5C	0.89	Re3—F7 <sup>viii</sup>	1.950 (6)
N6—H6A	0.89	Re3—F7 <sup>ix</sup>	1.950 (6)
N6—H6B	0.89	Re3—F7 <sup>x</sup>	1.950 (6)
N2—Co1—N6	89.7 (4)	F1—Re2—F4	178.1 (3)
N2—Co1—N1	89.0 (4)	F1—Re2—F5	88.7 (3)
N6—Co1—N1	90.0 (3)	F4—Re2—F5	91.0 (3)
N2—Co1—N3	90.2 (4)	F1—Re2—F6	92.3 (3)
N6—Co1—N3	178.6 (3)	F4—Re2—F6	89.6 (3)
N1—Co1—N3	88.6 (3)	F5—Re2—F6	91.3 (3)
N2—Co1—N5	179.4 (3)	F1—Re2—F3	87.9 (3)
N6—Co1—N5	90.7 (4)	F4—Re2—F3	90.2 (3)
N1—Co1—N5	90.6 (4)	F5—Re2—F3	87.6 (3)
N3—Co1—N5	89.4 (4)	F6—Re2—F3	178.9 (3)
N2—Co1—N4	91.5 (4)	F1—Re2—F2	89.8 (3)
N6—Co1—N4	91.2 (3)	F4—Re2—F2	90.5 (3)
N1—Co1—N4	178.7 (3)	F5—Re2—F2	178.5 (3)
N3—Co1—N4	90.2 (3)	F6—Re2—F2	88.6 (3)
N5—Co1—N4	88.9 (4)	F3—Re2—F2	92.5 (3)
Co1—N1—H1A	109.5	O2 <sup>i</sup> —Re1—O2	109.5 (3)
Co1—N1—H1B	109.5	O2 <sup>i</sup> —Re1—O2 <sup>ii</sup>	109.5 (3)
H1A—N1—H1B	109.5	O2—Re1—O2 <sup>ii</sup>	109.5 (3)
Co1—N1—H1C	109.5	O2 <sup>i</sup> —Re1—O1	109.5 (3)
H1A—N1—H1C	109.5	O2—Re1—O1	109.5 (3)
H1B—N1—H1C	109.5	O2 <sup>ii</sup> —Re1—O1	109.5 (3)
Co1—N2—H2A	109.5	F8 <sup>iii</sup> —Re4—F8 <sup>iv</sup>	90.5 (3)
Co1—N2—H2B	109.5	F8 <sup>iii</sup> —Re4—F8 <sup>ii</sup>	180.0 (3)
H2A—N2—H2B	109.5	F8 <sup>iv</sup> —Re4—F8 <sup>ii</sup>	89.5 (3)
Co1—N2—H2C	109.5	F8 <sup>iii</sup> —Re4—F8 <sup>v</sup>	90.5 (3)
H2A—N2—H2C	109.5	F8 <sup>iv</sup> —Re4—F8 <sup>v</sup>	90.5 (3)
H2B—N2—H2C	109.5	F8 <sup>ii</sup> —Re4—F8 <sup>v</sup>	89.5 (3)
Co1—N3—H3A	109.5	F8 <sup>iii</sup> —Re4—F8	89.5 (3)
Co1—N3—H3B	109.5	F8 <sup>iv</sup> —Re4—F8	89.6 (3)
H3A—N3—H3B	109.5	F8 <sup>ii</sup> —Re4—F8	90.5 (3)
Co1—N3—H3C	109.5	F8 <sup>v</sup> —Re4—F8	180.0
H3A—N3—H3C	109.5	F8 <sup>iii</sup> —Re4—F8 <sup>i</sup>	89.5 (3)
H3B—N3—H3C	109.5	F8 <sup>iv</sup> —Re4—F8 <sup>i</sup>	180.0
Co1—N4—H4A	109.5	F8 <sup>ii</sup> —Re4—F8 <sup>i</sup>	90.5 (3)
Co1—N4—H4B	109.5	F8 <sup>v</sup> —Re4—F8 <sup>i</sup>	89.5 (3)
H4A—N4—H4B	109.5	F8—Re4—F8 <sup>i</sup>	90.5 (3)
Co1—N4—H4C	109.5	F7 <sup>vi</sup> —Re3—F7 <sup>vii</sup>	91.0 (3)
H4A—N4—H4C	109.5	F7 <sup>vi</sup> —Re3—F7	89.0 (3)
H4B—N4—H4C	109.5	F7 <sup>vii</sup> —Re3—F7	89.0 (3)

Co1—N5—H5A	109.5	F7 <sup>vi</sup> —Re3—F7 <sup>viii</sup>	91.0 (3)
Co1—N5—H5B	109.5	F7 <sup>vii</sup> —Re3—F7 <sup>viii</sup>	91.0 (3)
H5A—N5—H5B	109.5	F7—Re3—F7 <sup>viii</sup>	180.0 (4)
Co1—N5—H5C	109.5	F7 <sup>vi</sup> —Re3—F7 <sup>ix</sup>	180.0
H5A—N5—H5C	109.5	F7 <sup>vii</sup> —Re3—F7 <sup>ix</sup>	89.0 (3)
H5B—N5—H5C	109.5	F7—Re3—F7 <sup>ix</sup>	91.0 (3)
Co1—N6—H6A	109.5	F7 <sup>viii</sup> —Re3—F7 <sup>ix</sup>	89.0 (3)
Co1—N6—H6B	109.5	F7 <sup>vi</sup> —Re3—F7 <sup>x</sup>	89.0 (3)
H6A—N6—H6B	109.5	F7 <sup>vii</sup> —Re3—F7 <sup>x</sup>	180.0
Co1—N6—H6C	109.5	F7—Re3—F7 <sup>x</sup>	91.0 (3)
H6A—N6—H6C	109.5	F7 <sup>viii</sup> —Re3—F7 <sup>x</sup>	89.0 (3)
H6B—N6—H6C	109.5	F7 <sup>ix</sup> —Re3—F7 <sup>x</sup>	91.0 (3)

Symmetry codes: (i)  $-x+y+1, -x+1, z$ ; (ii)  $-y+1, x-y, z$ ; (iii)  $y+1/3, -x+y+2/3, -z+5/3$ ; (iv)  $x-y+1/3, x-1/3, -z+5/3$ ; (v)  $-x+4/3, -y+2/3, -z+5/3$ ; (vi)  $x-y+2/3, x+1/3, -z+4/3$ ; (vii)  $y-1/3, -x+y+1/3, -z+4/3$ ; (viii)  $-x+2/3, -y+4/3, -z+4/3$ ; (ix)  $-x+y, -x+1, z$ ; (x)  $-y+1, x-y+1, z$ .

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1A $\cdots$ F1 <sup>vii</sup>	0.89	2.34	3.085 (11)	141
N1—H1A $\cdots$ F5 <sup>vii</sup>	0.89	2.29	3.078 (10)	148
N1—H1B $\cdots$ F5	0.89	2.32	3.037 (10)	138
N1—H1B $\cdots$ F7	0.89	2.42	3.098 (11)	133
N1—H1C $\cdots$ F3	0.89	2.40	3.144 (10)	141
N1—H1C $\cdots$ O1S <sup>ii</sup>	0.89	2.35	3.084 (12)	140
N2—H2A $\cdots$ F2 <sup>xi</sup>	0.89	2.46	3.243 (10)	148
N2—H2A $\cdots$ O2 <sup>xi</sup>	0.89	2.54	3.089 (12)	121
N2—H2B $\cdots$ F4	0.89	2.31	3.137 (12)	155
N2—H2B $\cdots$ F4 <sup>xi</sup>	0.89	2.58	3.161 (10)	124
N2—H2C $\cdots$ F7	0.89	2.08	2.928 (10)	158
N3—H3A $\cdots$ F6 <sup>ix</sup>	0.89	2.57	3.054 (10)	115
N3—H3A $\cdots$ O2S	0.89	2.26	3.027 (12)	145
N3—H3B $\cdots$ F5 <sup>ix</sup>	0.89	2.52	3.132 (10)	127
N3—H3B $\cdots$ F7	0.89	2.32	2.911 (11)	123
N3—H3C $\cdots$ F5 <sup>vii</sup>	0.89	2.24	3.112 (10)	166
N4—H4A $\cdots$ F2 <sup>xi</sup>	0.89	2.16	3.038 (10)	170
N4—H4A $\cdots$ F6 <sup>xi</sup>	0.89	2.57	3.126 (10)	121
N4—H4B $\cdots$ F6 <sup>ix</sup>	0.89	2.19	2.969 (10)	146
N4—H4C $\cdots$ F8 <sup>xii</sup>	0.89	2.21	3.019 (11)	150
N5—H5A $\cdots$ O2S	0.89	2.08	2.936 (12)	162
N5—H5B $\cdots$ F1 <sup>vii</sup>	0.89	2.20	3.057 (11)	162
N5—H5C $\cdots$ F1 <sup>ii</sup>	0.89	2.49	3.019 (11)	119
N5—H5C $\cdots$ F2 <sup>ii</sup>	0.89	2.43	3.261 (11)	157
N6—H6A $\cdots$ F4 <sup>xi</sup>	0.89	2.55	3.110 (10)	122
N6—H6A $\cdots$ F6 <sup>xi</sup>	0.89	2.16	3.037 (10)	168
N6—H6B $\cdots$ F2 <sup>ii</sup>	0.89	2.16	2.968 (10)	151

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N6—H6B···O1S <sup>ii</sup>	0.89	2.67	3.227 (11)	122
N6—H6C···F4	0.89	2.14	2.982 (10)	159

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Symmetry codes: (ii)  $-y+1, x-y, z$ ; (vii)  $y-1/3, -x+y+1/3, -z+4/3$ ; (ix)  $-x+y, -x+1, z$ ; (xi)  $-x+1, -y+1, -z+1$ ; (xii)  $-x+2/3, -y+1/3, -z+4/3$ .