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fac-Tricarbonyl[hydroxybis(2-pyridyl)methanolato-κ^3*N*,*O*,*N*′]rhenium(I)

Mohammed Bakir

Department of Chemistry, The University of the West Indies, Mona Campus, Kingston 7, Jamaica, West Indies
Correspondence e-mail: mbakir@uwimona.edu.jm

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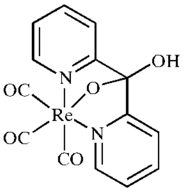
The Re^I centre in the title compound, [Re($C_{11}H_9N_2O_2$)(CO)$_3$] or *fac*-Re(CO)$_3$(dpkO,OH) [dpkO,OH is hydroxybis(2-pyridyl)methanolato], (I), is in a pseudo-octahedral environment in which the major distortion is due to the constraints associated with the tridentate binding of the dpkO,OH anion. The carbonyl groups are orthogonal, with an average C—Re—C angle of 90.2 (3)°. The molecules pack in stacks of antiparallel tapes of (I) interlocked *via* a network of hydrogen bonds.

Comment

Several examples of the addition of nucleophiles at the ketonic C atom of rhenium compounds of di-2-pyridyl ketone (dpk) have been reported (Bakir & McKenzie, 1997; Gerber *et al.*, 1995, 1993). Structural studies on ReOCl$_2$(dpkO,OH) (Gerber *et al.*, 1993) and *fac*-Re(CO)$_3$(dpk-o)Cl (dpk-o is di-2-pyridyl ketone oxime; Bakir, 2001) revealed a pseudo-octahedral coordination about Re in which the major distortion was due to the coordination of dpk-o/dpkO,OH. The structure of *fac*-Re(CO)$_3$(dpkO,OH), (I), is reported here and compared with the structures of rhenium compounds of dpk-o, dpkO,OH and other related compounds.



(I)

The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. The molecule adopts a pseudo-octahedral geometry about Re, with two N atoms and one O atom from the dpkO,OH anion and three C atoms from the carbonyl groups occupying the coordinated sites. The three carbonyl groups are orthogonal, with an average C—Re—C angle of 90.2 (3)°.

The Re—C bond distances to the carbonyl groups (Table 1) are longer for the carbonyl groups *trans* to the pyridine rings than for the carbonyl group *trans* to the oxo group. The elongation of the Re—C bonds *trans* to the pyridine rings may be due to the π acidity of the pyridine rings and the increased bond strength of the Re—N bond due to its synergic bonding, whilst the decrease in the Re—C bond *trans* to the oxo group may be due to the π donation of the oxo group and increased electron density around the Re atom. This variation in Re—C bond distances is consistent with the three carbonyl stretching bands observed in the IR spectrum (Bakir & McKenzie, 1997). The distances are similar to those observed in a variety of rhenium carbonyl compounds of the type *fac*-Re(CO)$_3$(*L*–*L*)*X*, where *L*–*L* is dpk-o (Bakir, 2001), and other related α-diimine ligands (Xue *et al.*, 1998; Horn & Snow, 1980). For example, in *fac*-Re(CO)$_3$(dpk-o)Cl, the average Re—C bond distance is 1.91 (6) Å and the average C—Re—C angle is 88.5 (6)° (Bakir, 2001).

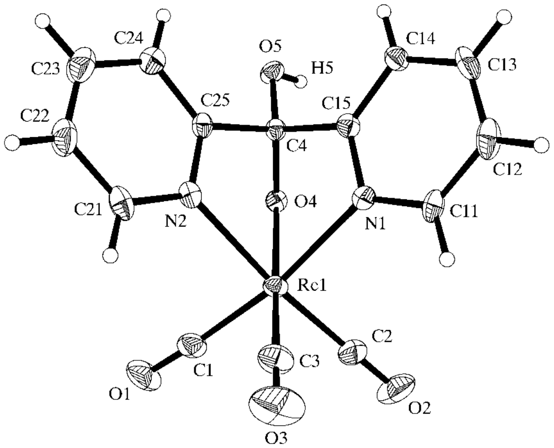


Figure 1
A view of the molecule of (I), with displacement ellipsoids drawn at the 30% probability level and H atoms shown as small spheres of arbitrary radii.

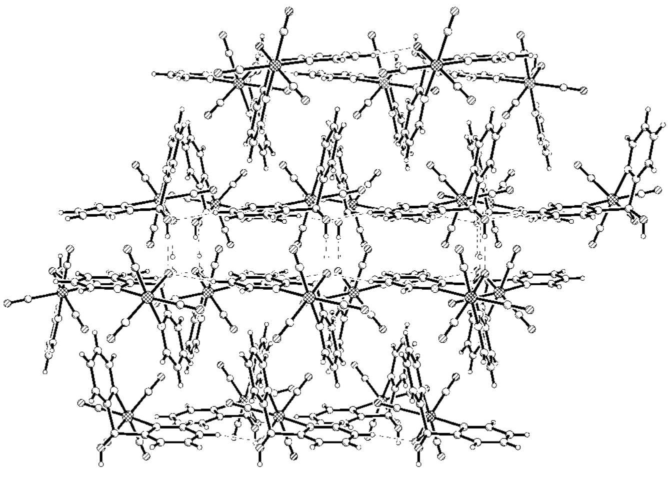


Figure 2
A packing diagram for (I).

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The distortion from octahedral geometry in (I) is due to the constraints associated with the tridentate chelation of dpkO,OH, as is apparent from the N—N and N—O bite angles (Table 1). The coordinated dpkO,OH anion forms a six-membered metallocyclic ring (Re1/N1/C15/C4/C25/N2) and two five-membered metallocyclic rings (Re1/N*n*/C*n*5/C4/O4, where *n* = 1 or 2) fused along the Re1—O4—C4 junction, with the pyridine rings bent away from the chelating oxide anion. This arrangement leaves one pyridine ring in the equatorial plane and the other in the axial plane, and the oxide atom (O4) and hydroxy group (O5—H5) exposed for potential intermolecular interactions.

The N—Re—N bite angle of 81.6 (2)° for the coordinated dpkO,OH is of the same order as the angle of 80.3 (2)° for dpk-o in *fac*-$Re(CO)_3$(dpk-o)Cl (Bakir, 2001), smaller than the value of 84.6 (4)° reported for dpkO,OH in $ReOCl_2$(dpkO,OH) (Gerber *et al.*, 1993) and larger than the value of 74.3 (4)° reported for bipy in *fac*-$Re(CO)_3$(bipy)($OPOF_2$) (bipy is 2,2′-bipyridine; Horn & Snow, 1980). These results confirm that the five-membered metallocyclic rings in rhenium compounds of α-diimine ligands are more constrained than the six-membered metallocyclic rings.

The Re—O and Re—N bond distances in (I) (Table 1) are slightly longer than those reported for high-valent $ReOCl_2$(dpkO,OH), which is consistent with the change in Re oxidation state. The steric constraints imposed on the tridentate dpkO,OH anion in both high- and low-valent rhenium compounds are severe and are associated with the N/O five-membered metallocyclic rings.

The packing of (I) (Fig. 2) shows stacks of interlocked antiparallel tapes of (I) in which the oxide atom (O4) and the hydroxy group (H5—O5) from adjacent stacks are face-to-face (Fig. 3). This arrangement leads to the formation of classical O···H—O hydrogen bonds between adjacent stacks, and non-classical C—H···O hydrogen bonds between atom H12 on the equatorial pyridine ring and the adjacent chelating axial oxide atoms (O4) in each tape (Fig. 3). The bond distances and angles for these hydrogen bonds (Table 2) are similar to those reported for *fac*-$Re(CO)_3$(dpk-o)Cl, $ReOCl_2$(dpkO,OH) and other compounds containing such bonds. For example, in *fac*-$Re(CO)_3$(dpk-o)Cl (Bakir, 2001), hydrogen-bond parameters of 0.93, 2.50, 3.21 (9) Å, and 133° were observed for the soft non-classical C21—H21···O5 hydrogen bond, and parameters of 0.82, 1.88, 2.681 (9) Å, and 164° were observed for the classical O4—H4···O5 hydrogen bond.

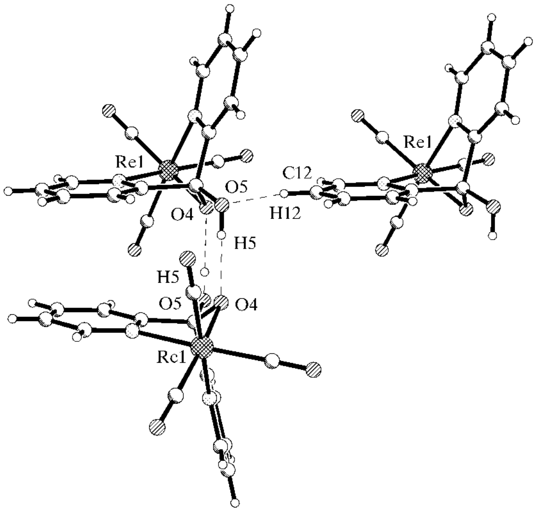

Figure 3
The classical and non-classical hydrogen bonds in (I).

Due to interest in their rich physico-chemical properties, reactivity patterns and application in molecular sensing, work is now in progress to grow crystals of a variety of free bipyridyl-like ligands and their metal compounds in order to explore their solid-state structures, conformations and electro-optical properties.

Experimental

Compound (I) was synthesized as described previously by Bakir & McKenzie (1997). The CH_3CN used for crystallization was of reagent grade and was thoroughly deoxygenated prior to use. When (I) was allowed to stand in CH_3CN for several days at room temperature, yellow crystals of (I) were obtained. A single crystal was selected and mounted on a glass fibre with epoxy cement, and used for data collection.

Crystal data

$[Re(C_{11}H_9N_2O_2)(CO)_3]$
$M_r = 471.43$
Monoclinic, $C2/c$
$a = 27.742$ (2) Å
$b = 7.8344$ (16) Å
$c = 16.2658$ (18) Å
$\beta = 125.679$ (5)°
$V = 2871.7$ (7) Å^3
$Z = 8$
$D_x = 2.181$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 23 reflections
$\theta = 6.3$–26.4°
$\mu = 8.49$ mm^{-1}
$T = 298$ (2) K
Rectangular, yellow
0.4 × 0.3 × 0.2 mm

Data collection

Bruker *P*4 diffractometer
$2\theta/\omega$ scans
Absorption correction: empirical *via* ψ scan (*XSCANS*; Siemens, 1996)
$T_{min} = 0.061$, $T_{max} = 0.183$
3138 measured reflections
2535 independent reflections
2359 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 25°$
$h = -1 \rightarrow 32$
$k = -1 \rightarrow 9$
$l = -19 \rightarrow 15$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.093$
$S = 1.02$
2535 reflections
200 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.075P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.75$ e Å^{-3}
$\Delta\rho_{min} = -1.34$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.00143 (11)

H atoms were assigned by assuming idealized geometry, with O—H and C—H distances of 0.82 and 0.93 Å, respectively. The position of atom H5 was confirmed in a difference Fourier map, and was then fixed and allowed to ride on atom O5. In the final refinement, two peaks with residual electron density greater than 1 e Å^{-3} appeared at distances of 1.21 and 1.15 Å from Re1. The deepest hole, with an electron density of −1.34 e Å^{-3}, appeared at 1.42 Å from Re1.

Table 1
Selected geometric parameters (Å, °).

Re1—C3	1.904 (6)	C1—O1	1.122 (8)
Re1—C2	1.936 (6)	C2—O2	1.129 (8)
Re1—C1	1.942 (6)	C3—O3	1.159 (7)
Re1—O4	2.108 (3)	C4—O5	1.379 (6)
Re1—N1	2.175 (4)	C4—O4	1.413 (6)
Re1—N2	2.192 (5)		
C3—Re1—C2	88.3 (3)	C1—Re1—N2	91.4 (2)
C3—Re1—C1	90.2 (3)	O4—Re1—N2	75.26 (14)
C2—Re1—C1	92.1 (3)	N1—Re1—N2	81.61 (17)
C3—Re1—O4	170.6 (2)	O1—C1—Re1	176.8 (6)
C2—Re1—O4	98.05 (19)	O2—C2—Re1	179.4 (7)
C1—Re1—O4	96.48 (18)	O3—C3—Re1	177.2 (6)
C3—Re1—N1	98.2 (2)	O5—C4—O4	113.3 (4)
C2—Re1—N1	94.0 (2)	O5—C4—C15	113.6 (4)
C1—Re1—N1	169.8 (2)	O4—C4—C15	106.7 (4)
O4—Re1—N1	74.55 (14)	O5—C4—C25	108.7 (4)
C3—Re1—N2	98.0 (2)	O4—C4—C25	107.4 (4)
C2—Re1—N2	172.74 (19)	C4—O4—Re1	105.2 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O5—H5···O4^{i}	0.82	1.86	2.679 (5)	179
C12—H12···O4^{ii}	0.93	2.26	3.183 (7)	171

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

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1212). Services for accessing these data are described at the back of the journal.

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