metal-organic papers

cis-Dicarbonyl(hydroxydi-2-pyridylmethanolato-κ^3N,O,N')(triphenylphosphine-κP)rhenium(I) dimethyl sulfoxide hemisolvate

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The title compound, $[\text{Re}(\text{C}_{11}\text{H}_9\text{N}_2\text{O}_2)(\text{C}_{18}\text{H}_{15}\text{P})(\text{CO})_2]\cdot 0.5\text{C}_2\text{H}_6\text{OS}$ or *cis*-[Re(CO)$_2$(PPh$_3$)(dpkO,OH)]·0.5dmso (dpk-O,OH is hydroxydi-2-pyridylmethanolate and dmso is dimethyl sulfoxide), obtained from a dmso solution of *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] (dpk is di-2-pyridylmethanone), crystallizes in the monoclinic space group $P2_1/c$, with two independent *cis*-[Re(CO)$_2$(PPh$_3$)(dpkO,OH)] complexes and one dmso molecule in the asymmetric unit. These results confirm the facile hydrolysis of *N,N*-coordinated di-2-pyridyl methanone to form a hydroxytris(2-pyridyl) methanolato-κ^3N,O,N' coordinated anion. The coordinated atoms are in a pseudo-octahedral geometry, with the major distortion from octahedral geometry being due to the constraints associated with the κ^3N,O,N' binding of the hydroxytris(2-pyridyl)-methanolate anion. The methyl groups of the dmso molecule show orientational disorder and have an insignificant effect on the overall precision and geometry. The molecular packing shows stacks of molecular units interlocked *via* a network of classical intramolecular O—H$\cdots$O hydrogen bonds, which link the complexes into pairs, and non-classical intermolecular C—H$\cdots$O hydrogen bonds, which link the various stacks.

Comment

The ligand di-2-pyridylmethanone (dpk) and its oxime and hydrazone derivatives are of interest, in part because of their physicochemical properties, reactivity patterns, and applications in many areas, including catalysis, sensors, pharmaceuticals, microelectronics and others (Bernhardt *et al.*, 2003; Camel, 2003; Crowder *et al.*, 2004; Kepert *et al.*, 2004; Kumagai *et al.*, 2003; Sreekanth *et al.*, 2003; Swearingen *et al.*, 2002; Terra *et al.*, 2002). Upon coordination to a variety of metal atoms, dpk undergoes facile hydrolysis to form a *gem*-diol, which allows for the expansion of monodentate (di-2-pyridylmethanone-κ^1N or -κ^1O) or bidentate (di-2-pyridyl-methanone-κ^2N,N') coordination of dpk to tridentate [hydroxytris(2-pyridyl)methanolato-κ^3N,O,N'; Bakir & McKenzie, 1997; Gerber *et al.*, 1995] and tetradentate [tris(2-pyridyl)methandiolato-κ^4N,O,N',O] binding (Papaefstathiou *et al.*, 2002). We have been interested in the chemistry of polypyridyl-like compounds of the type (C$_5$H$_4$N)$_2X$, where $X =$ CO, C = N—OH or C = NH—N*R*, and have reported on the synthesis and spectroscopic, electrochemical and structural properties of a series of dpk derivatives and their metal complexes (Bakir & McKenzie, 1997; Bakir, Brown & Johnson, 2004; Bakir, Hassan *et al.*, 2004; Bakir & Brown, 2003; Bakir *et al.*, 2003; Bakir, 2002*a,b,c*; Bakir, 2001*a,b*). Although we have reported on the solid-state structural analysis of the rhenium tricarbonyl complex with hydroxytris(2-pyridyl)methanolato-κ^3N,O,N', *fac*-[Re(CO)$_3$(dp-

kO,OH)], to our knowledge there has been no report to date on the solid-state structure of metal dicarbonyl compounds of hydroxydi-2-pyridylmethanolato-$\kappa^3 N,O,N'$ (Bakir, 2002c). In this report, the structure of the title dimethylsulfoxide solvated compound, cis-[Re(CO)$_2$(PPh$_3$)(dpkO,OH)]·-0.5dmso, (I), is described and compared with the structures of rhenium complexes with α-diimine ligands and hydroxy-di-(2-pyridyl)methoxide (dpkO,OH) and other related compounds.


(I)
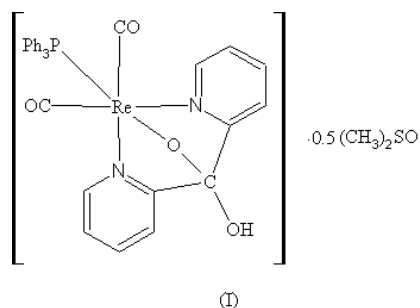
When cis-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] was allowed to stand in dmso at room temperature, yellow crystals of cis-[Re(CO)$_2$(PPh$_3$)($\kappa^3 N,O,N'$-dpkO,OH)]·0.5dmso, (I), suitable for X-ray analysis were obtained. The facile hydrolysis of N,N-bidentate dpk in cis-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] is similar to that reported for the hydrolysis of N,N-coordinated dpk in fac-[Re(CO)$_3$(dpk)Cl] and other metal complexes containing N,N-bidentate dpk (Bakir & McKenzie, 1997; Gerber et al., 1995).

A view of the asymmetric unit of (I) (Figs. 1 and 2) reveals the presence of two cis-[Re(CO)$_2$(PPh$_3$)($\kappa^3 N,O,N'$-dpkO,-OH)] molecules along with one solvent molecule (dmso). The coordination about Re is pseudo-octahedral, with two N atoms from the pyridyl rings, two C atoms from the carbonyl groups, one O atom from the methanolate group and a P atom occupying the coordinating sites. The distortion from octahedral geometry in the molecule of (I) is due to the tridentate binding of hydroxydi-2-pyridylmethanolato-$\kappa^3 N,O,N'$ to form a six-membered metallocyclic ring (N1/C15/C3/C25/N2/Re) and two five-membered metallocyclic rings (N1/C15/C3/O3/Re) fused along the Re—O3—C3 junction, and is apparent from the N,N and N,O bite angles of hydroxydi-2-pyridylmethanolato-$\kappa^3 N,O,N$ (Table 1). This is similar to what was reported for the tridentate binding of the hydroxydi-2-pyridylmethanolato-$\kappa^3 N,O,N'$ anion in fac-[Re(CO)$_3$-($\kappa^3 N,O,N'$-dpkO,OH)], [ReOCl$_2$($\kappa^3 N,O,N'$-dpkO,OH)], and other related compounds (Bakir & McKenzie, 1997; Bakir, 2002c; Gerber et al., 1995). With the exception of the C2'—Re'—C1' bond angle, the bond distances and angles of the coordinated atoms (Table 1) are normal and of the same order as those reported for a variety of compounds containing such bonds (Bakir, 2002c; Bakir, 2001a,b; Gerber et al., 1995, 1993). For example, an N—Re—N bite angle of 81.6 (2)°, N—Re—O bite angles of 74.55 (14) and 75.26 (14)°, and an average C—Re—C angle of 90.2 (3)° were observed in fac-[Re(CO)$_3$($\kappa^3 N,O,N'$-dpkO,OH)] (Bakir, 2002c).
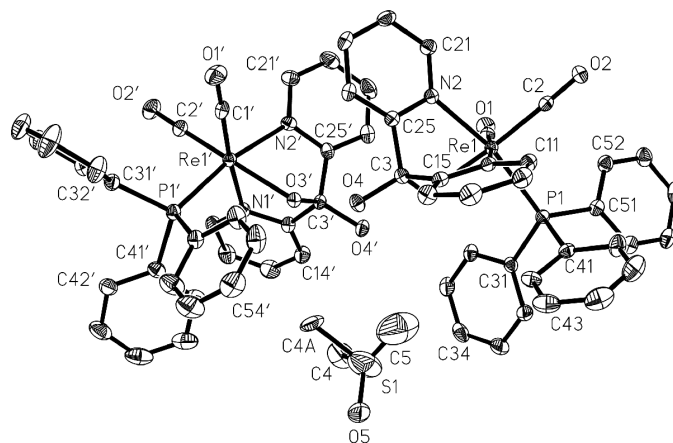
Figure 1
A view of the asymmetric unit of (I). H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 20% probability level.
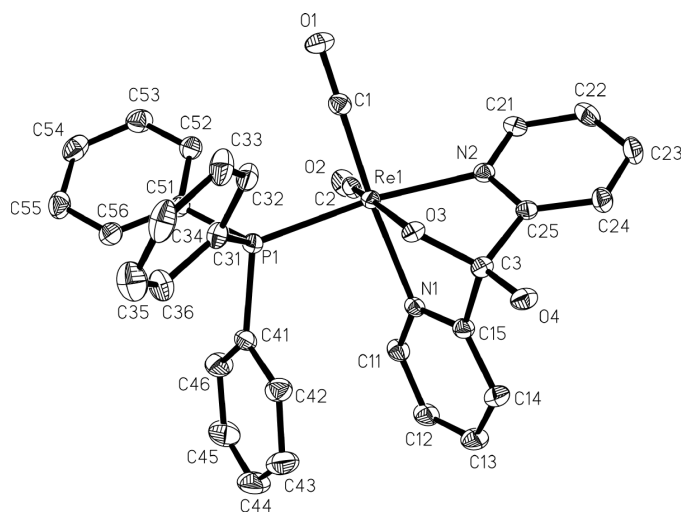
Figure 2
A drawing of one molecule of the cis-[Re(CO)$_2$(PPh$_3$)($\kappa^3 N,O,N'$-dpkO,OH)] complex of (I); the second molecule and the solvent have been omitted.

The methyl groups of the dmso molecule show disorder, which is manifest in or modelled by the presence of extra residual electron density near S1, the presence of solvent voids, the splitting of one methyl group into two positions, residual effects of absorption or a series of termination or other factors. Attempts to model the disorder of the dmso (see Experimental) gave best results when the peaks ~1.6 Å from S1 were assigned to one methyl group with an occupancy of 57% for the major site.

The packing of molecules of (I) shows stacks of cis-[Re(CO)$_2$(PPh$_3$)($\kappa^3 N,O,N'$-dpkO,OH)]·0.5dmso molecules interlocked via a network of hydrogen bonds (Fig. 3 and Table 2) and reveals classical O—H⋯O intermolecular hydrogen bonds between the methanolate groups of adjacent cis-[Re(CO)$_2$(PPh$_3$)($\kappa^3 N,O,N'$-dpkO,OH)] units to form an eight-membered (O3/C3/O4/H1/O3'/C3'/O4'/H1') ring in a boat conformation, forming cis-[Re(CO)$_2$(PPh$_3$)($\kappa^3 N,O,N'$-dpkO,OH)] hydrogen-bonded dimers (Fig. 4). Non-classical C—H⋯O hydrogen bonds connect the different stacks. The

distances and angles of the hydrogen bonds are of the same order as those reported for the same types of bonds in *fac*-[Re(CO)$_3$($\kappa^3 N,O,N'$-dpkO,OH)] (Bakir, 2001*c*). For example, hydrogen-bond parameters of 0.82, 1.86, 2.679 (5) Å and 179° were reported for the O—H···O hydrogen bond, and parameters of 0.93, 2.26, 3.183 (7) Å and 171° were observed for the non-classical C—H···O hydrogen bond (Bakir, 2002*c*).

In conclusion, crystal-growth and structural studies of (I) confirm the facile hydrolysis of coordinated di-2-pyridylmethanone and the sensitivity of the hydrolysed product to its surroundings, as apparent from the incorporation of a solvent dmso molecule in the resulting crystal structure. Structural analysis reveals pseudo-octahedral coordination around Re and pseudo-tetrahedral geometry about S, and the presence of a network of hydrogen bonds that may account for the stability of the hydrolysed product.

Due to their convenient synthesis and rich physicochemical properties, together with our continued interest in the development of molecular sensors, the coordination chemistry and sensing behaviour of di-2-pyridylmethanone and its derivatives remain under investigation in our laboratories.

Experimental

The compound *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] was prepared by refluxing a mixture of di-2-pyridylmethanone, [Re(CO)$_5$Cl] and PPh$_3$ in dry toluene, as described earlier by Bakir & McKenzie (1997). Single crystals of (I) were obtained from a dmso solution of *cis*-[Re(CO)$_2$(PPh$_3$)(dpk)Cl] when allowed to stand at room temperature for several days.

Crystal data

[Re(C$_{11}$H$_9$N$_2$O$_2$)(C$_{18}$H$_{15}$P)-(CO)$_2$]·0.5C$_2$H$_6$OS	$D_x = 1.629$ Mg m^{-3}
$M_r = 744.77$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 45 reflections
$a = 17.336$ (2) Å	$\theta = 1.9$–17.6°
$b = 16.5870$ (19) Å	$\mu = 4.13$ mm^{-1}
$c = 21.125$ (3) Å	$T = 293$ (2) K
$\beta = 91.127$ (10)°	Block, yellow
$V = 6073.4$ (13) Å^3	$0.5 \times 0.4 \times 0.3$ mm
$Z = 8$	

Data collection

Bruker *P*4 diffractometer	$R_{int} = 0.025$
$2\theta/\omega$ scan	$\theta_{max} = 25.0°$
Absorption correction: ψ scan (*XSCANS* in *SHELXTL*; Bruker, 1997)	$h = -1 \rightarrow 20$
	$k = -19 \rightarrow 1$
	$l = -25 \rightarrow 25$
$T_{min} = 0.152$, $T_{max} = 0.290$	3 standard reflections
12 608 measured reflections	every 97 reflections
10 614 independent reflections	intensity decay: none
8772 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 7.9122P]$
$R[F^2 > 2\sigma(F^2)] = 0.034$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.080$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.02$	$\Delta\rho_{max} = 1.08$ e Å^{-3}
10614 reflections	$\Delta\rho_{min} = -1.23$ e Å^{-3}
751 parameters	Extinction correction: none
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Re1—C1	1.871 (5)	N1′—C11′	1.338 (7)
Re1—C2	1.874 (6)	C15′—C3′	1.525 (7)
Re1—O3	2.137 (3)	C3′—O4′	1.395 (6)
Re1—N2	2.169 (4)	C3′—C25′	1.523 (7)
Re1—N1	2.200 (4)	P1′—C41′	1.829 (6)
Re1—P1	2.3662 (14)	C31—C36	1.382 (8)
O1—C1	1.184 (6)	C51—C56	1.399 (8)
O2—C2	1.173 (6)	S1—O5	1.471 (5)
O3—C3	1.398 (6)	S1—C4A	1.529 (13)
N1—C15	1.343 (7)	S1—C4	1.551 (18)
Re1′—C2′	1.869 (6)	C36′—C31′	1.384 (8)
Re1′—C1′	1.877 (6)	O4—C3	1.391 (6)
Re1′—O3′	2.134 (3)	C15—C14	1.378 (7)
Re1′—N2′	2.161 (4)	C15—C3	1.525 (7)
Re1′—N1′	2.204 (4)	C3—C25	1.533 (7)
Re1′—P1′	2.3756 (15)	C13—C12	1.364 (9)
C2′—O2′	1.177 (7)	C13—C14	1.402 (8)
C1′—O1′	1.169 (7)		
O3′—C3′	1.388 (6)		
C1—Re1—C2	89.6 (2)	O4′—C3′—C25′	113.1 (4)
C1—Re1—O3	101.30 (19)	O3′—C3′—C15′	108.3 (4)
C2—Re1—O3	167.52 (18)	O4′—C3′—C15′	107.4 (4)
C1—Re1—N2	94.8 (2)	C25′—C3′—C15′	105.6 (4)
C1—Re1—N1	174.8 (2)	C41′—P1′—C51′	99.0 (3)
O3—Re1—N1	74.67 (14)	C51—P1—C31	102.1 (2)
N2—Re1—N1	81.04 (15)	C56—C51—C52	116.4 (5)
C1—Re1—P1	90.23 (17)	C53—C52—C51	122.2 (6)
O3—Re1—P1	92.69 (10)	O5—S1—C4A	117.1 (7)
N2—Re1—P1	167.07 (11)	O5—S1—C4	120.5 (9)
C11—N1—C15	118.9 (4)	C4A—S1—C4	121.7 (10)
C21—N2—C25	118.6 (5)	O5—S1—C5	103.1 (6)
C21—N2—Re1	128.6 (4)	C4A—S1—C5	88.1 (9)
C2′—Re1′—C1′	86.3 (2)	C4—S1—C5	87.2 (11)
C2′—Re1′—O3′	166.67 (19)	O2—C2—Re1	175.9 (5)
C1′—Re1′—O3′	104.62 (19)	N1—C15—C14	122.5 (5)
C2′—Re1′—N2′	97.2 (2)	N1—C15—C3	112.2 (4)
O3′—Re1′—N2′	74.81 (14)	C14—C15—C3	125.2 (5)
C2′—Re1′—N1′	94.0 (2)	O4—C3—O3	114.2 (4)
N2′—Re1′—N1′	81.11 (16)	O4—C3—C15	108.4 (4)
N2′—Re1′—P1′	168.94 (12)	O3—C3—C15	107.9 (4)
O2′—C2′—Re1′	175.7 (5)	O4—C3—C25	112.8 (4)
O1′—C1′—Re1′	175.3 (5)	O3—C3—C25	107.0 (4)
C3′—O3′—Re1′	104.4 (3)	C56′—C51′—C52′	117.5 (6)
C11′—N1′—C15′	119.5 (5)	C56—C55—C54	119.6 (6)
C11′—N1′—Re1′	128.3 (4)	C42′—C41′—C46′	118.7 (6)
O3′—C3′—O4′	114.4 (4)	O1—C1—Re1	179.6 (5)
O3′—C3′—C25′	107.6 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O4′—H4O′···O3	0.82	1.86	2.683 (5)	175
O4—H4O···O3′	0.82	1.87	2.679 (5)	167
C22′—H22′···O5[i]	0.93	2.44	3.256 (9)	146
C36—H36···O5[ii]	0.93	2.40	3.237 (8)	151
C43—H43···O1[iii]	0.93	2.57	3.365 (8)	144
C43′—H43′···O5[iv]	0.93	2.36	3.286 (10)	173

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

The refinement reveals an orientational disorder in the dmso solvent. In the final least-squares cycles with all atoms refined anisotropically, and with two methyl groups assigned to dmso, each at 100% occupancy, two peaks of 1.43 (4) and 1.09 (4) e Å^{-3} appeared near S1 and Re1′, respectively, and an R_1 value of 0.035 and a wR_2 value of 0.087 were observed. This model gave displacement parameters greater than 0.9 for atom C4 and an S1—C4 bond distance of
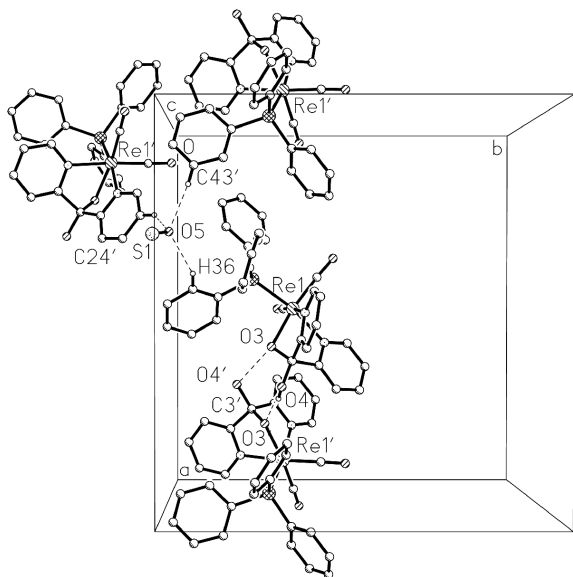
Figure 3
A view of the hydrogen bonds in (I) (dashed lines). For clarity, all H atoms except those involved in hydrogen bonding have been omitted. Symmetry codes used to generate equivalent atoms are as given in Table 2.
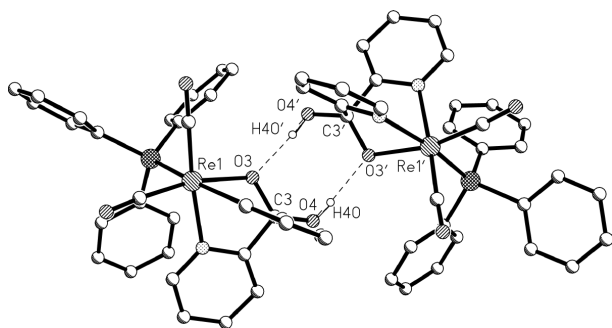
Figure 4
A view of the classical hydrogen bonds in (I) (dashed lines). For clarity, all H atoms except those involved in hydrogen bonding have been omitted. Symmetry codes used to generate equivalent atoms are as given in Table 2.

less than 1.6 Å. Attempts to restrain the S1—C4 bond distance and refine atoms C4 and C5 isotropically gave an R_1 value of 0.036 and a wR_2 value of 0.092. This led us to consider a new model, in which atoms C4 and C5 and their associated H atoms were eliminated, and a new refinement gave an R_1 value of 0.039 and a wR_2 value of 0.10. The resulting electron-density map shows three peaks near S1, with two ~1.6 Å and one ~1.9 Å from S1. The peaks at ~1.6 Å were assigned to C4 and C4A, with an initial site occupancy of 60% for C4 and 40% for C4A, and the peak at ~1.84 Å was assigned to C5. The addition of H atoms and refinement with anisotropic parameters for all non-H atoms without any restraint gave an R_1 value of 0.034 and a wR_2 value of 0.079, with S1—C4 and S1—C4A bond distances ~0.3 Å shorter than S1—C5. This model gave displacement parameters less than 0.25 for C atoms of the dmso, and only one peak with residual electron density of ~1.04 e Å^{-3} appeared near Re1′. Attempts to restrain the S1—C4 and S1—C4A bonds to 1.8 Å gave an R_1 value of 0.034 and an R_2 value of 0.083. The SQUEEZE algorithm in *PLATON* (http://www.cryst.chem.uu.nl/PLATON/p100303.html; Spek, 2003; van der Sluis & Spek, 1990) was invoked to calculate the solvent-accessible areas and voids and to filter the contribution of the distorted region.

In the absence of dmso, R_1 and wR_2 values of 0.072 and 0.182, respectively, were obtained after the least-squares cycles before application of the SQUEEZE algorithm. After application of the SQUEEZE algorithm, R_1 and wR_2 values of 0.0315 and 0.0754, respectively, were obtained. Although the SQUEEZE model shows improvement in the absence of dmso, this model was not used in the final data analysis because it eliminates the solvent contribution. All H atoms were assigned by assuming idealized geometry, with C—H distances of 0.96, 0.93 and 0.82 Å for primary CH₃, aromatic CH and OH, respectively, and they were treated as riding, with $U_{iso}(H) = 1.5U_{eq}(C,N,O)$.

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