

The first pyridyl *N,N'*-coordinated di-2-pyridyl ketone oxime, *fac*-tricarbonylchloro(di-2-pyridyl ketone oxime)rhenium(I) dimethyl sulfoxide solvate

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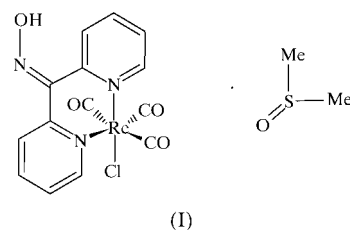
The structure of the first metal compound of pyridyl *N,N'*-coordinated di-2-pyridyl ketone oxime (dpk-o), *fac*-tricarbonylchloro(di-2-pyridyl-*κ**N* ketone oxime)rhenium(I) dimethyl sulfoxide solvate, $[\text{ReCl}(\text{C}_{11}\text{H}_9\text{N}_2\text{O})(\text{CO})_3] \cdot \text{C}_2\text{H}_6\text{OS}$, (I), is reported. The coordinated atoms (two N atoms from the pyridyl rings, three C atoms from the carbonyl groups and one Cl atom) are in a distorted octahedral arrangement, with the major distortion being due to the constraints associated with the binding of dpk-o. The packing of the molecules shows antiparallel tapes of (I), with a network of classical ($\text{O} \cdots \text{H}-\text{O}$) and non-classical ($\text{O} \cdots \text{H}-\text{C}$) hydrogen bonds between the dimethyl sulfoxide solvate molecule and the complexed metal moiety.

Comment

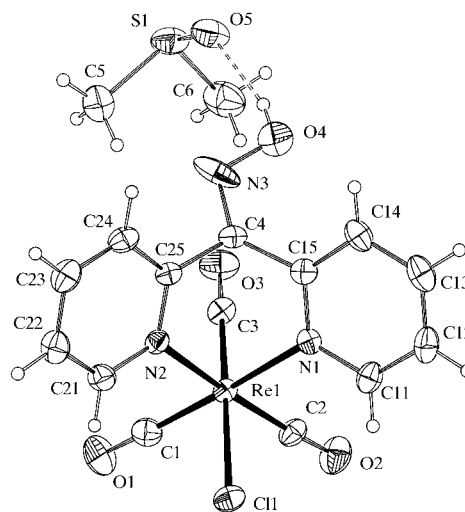
Oximes and their metal complexes have attracted considerable research interest due to their rich physicochemical properties, reactivity patterns and applications in many important chemical processes (Adams, 2000; Kuznetsov *et al.*, 2000). Although a variety of metal complexes of oximes have been reported, reports of complexes of dipyridyl and dipyridyl-like oximes are scarce (Adams, 2000; Bakir, 1999). Eight structures have been reported for the coordination of di-2-pyridyl ketone oxime (dpk-o) (Goher & Mautner, 1999; Jensen *et al.*, 1997; Psomas *et al.*, 1998; Schlemper *et al.*, 1990; Stemmler *et al.*, 1995; Sommerer *et al.*, 1995, 1997). In these reports, dpk-o is coordinated to the metal centre in a monodentate manner through an N atom of one pyridyl ring, as in $[\text{Ag}(\text{dpk-o})\text{NO}_2]$ (Sommerer *et al.*, 1995), in a bidentate manner through an N atom of one pyridyl ring and the N atom of the oxime moiety, as in $[\text{Co}(\text{dpkO,OH})(\text{dpk-o})]\text{NO}_2 \cdot \text{H}_2\text{O}$ [dpkO,OH is hydroxydi(2-pyridyl)methoxide; Jensen *et al.*, 1997], and in a tridentate manner through combined monodentate and bidentate binding, as in the case of the Cu^{I} dimer $[\text{CuCl}(\text{dpk-o}) \cdot \text{H}_2\text{O}]_2$ (Goher & Mautner, 1999). No evidence

for *N,N*-dipyridyl coordination of dpk-o has been noted to date.

The synthesis, optical and electrochemical behaviour of rhenium–tricarbonyl compounds of pyridyl *N,N'*-coordinated di-2-pyridyl ketone (dpk) and its oxime (dpk-o) and hydrazone (dpknph), where dpknph is di-2-pyridyl ketone *p*-nitrophenylhydrazone, have previously been reported by us (Bakir, 1997; Bakir & McKenzie, 1997*a,b*; Bakir, 1999; Bakir & Abdur-Rashid, 1999; Bakir *et al.*, 2000). These compounds exhibit rich electro-optical and optical properties, and their electrochemical and optical-sensing properties have been reported. In the case of dpk-o, electrochemical mechanisms for the oxidation and reduction of free and rhenium-coordinated dpk-o have been reported (Bakir, 1999). In the present report, the structure of the dimethyl sulfoxide-solvated title complex, (I), is described and compared with the structures of the rhenium compounds of α -diimine ligands and hydroxydi(2-pyridyl)methoxide (dpkO,OH).



The molecular structure of (I) is shown in Fig. 1, and selected bond distances and angles are given in Table 1. Two N atoms from the pyridyl rings, three C atoms from the carbonyl groups and one Cl atom occupy the coordination sites. The three carbonyl groups are in facial positions and are orthogonal, with an average C–Re–C angle of $88.47(3)^\circ$. The Re–C bond distances of the carbonyl groups (Table 1), with an average value of $1.91(7) \text{ \AA}$, are normal and similar to those reported for a variety of rhenium–carbonyl compounds of the type *fac*- $[\text{Re}(\text{CO})_3(\text{L}-\text{L})\text{X}]$, where L–L is an α -diimine ligand


Figure 1

The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

(Xue *et al.*, 1998; Horn & Snow, 1980). For example, in *fac*-[Re(CO)₃(bipy)(OPOF₂)], the average Re—C distance is 1.91 (2) Å and the average C—Re—C angle is 87.2 (8)° (Horn & Snow, 1980).

The distortion from octahedral geometry in (I) is due to the constraints associated with the binding of the dpk-o moiety, as is apparent from its N—Re—N bite angle of 80.27 (19)°. The coordinated dpk-o forms a six-membered Re1/N1/C15/C4/C25/N2 metallocyclic ring, with the pyridine rings in a butterfly formation. This arrangement leaves one pyridine ring in the equatorial plane, the other in the axial plane and the oxime moiety exposed for potential intermolecular interaction. The N—Re—N bite angle of the coordinated dpk-o moiety in (I) is smaller than the value of 84.6 (4)° reported for [ReOCl₂(dpkO,OH)] (Gerber *et al.*, 1993, 1993) and larger than the value of 74.3 (2)° in *fac*-[Re(CO)₃(bipy)(OPOF₂)] (Horn & Snow, 1980). These results show that the five-membered Re/N1/C15/C25/N2 rings of α -diimine ligands are more constrained than the six-membered Re1/N1/C15/C4/C25/N2 ring of dpk-o.

The packing of the molecules shows stacks of antiparallel tapes of (I), with a network of hydrogen bonds between the dimethyl sulfoxide solvate and adjacent *fac*-[Re(CO)₃(dpk-o)-Cl] molecules (Fig. 2 and Table 2). The bond distances and angles of the hydrogen bonds are of the same order as those observed in a variety of compounds containing such bonds (Gerber *et al.*, 1993; Glusker *et al.*, 1994; Batchelor *et al.*, 2000).

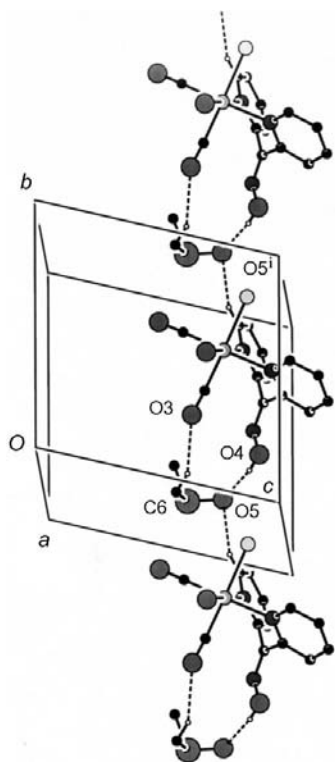


Figure 2
A view showing the chain of molecules linked by O—H...O and C—H...O hydrogen bonds extending in the *b* direction [symmetry code: (i) *x*, 1 + *y*, *z*]. For clarity, all H atoms except those involved in hydrogen bonding have been omitted.

Owing to their rich physicochemical properties and reactivity patterns, work is in progress to prepare a variety of metal compounds of dpk-o, to explore their solid-state structures and electro-optical properties.

Experimental

fac-[Re(CO)₃(dpk-o)Cl] was synthesized as described earlier by Bakir (1999). The dimethyl sulfoxide used for the crystallization was reagent grade and thoroughly deoxygenated prior to use. When *fac*-[Re(CO)₃(dpk-o)Cl] was allowed to stand in dimethyl sulfoxide for several days at room temperature, yellow crystals of (I) were obtained.

Crystal data

[ReCl(C ₁₁ H ₉ N ₂ O)(CO) ₃].C ₂ H ₆ OS	<i>Z</i> = 2
<i>M_r</i> = 583.02	<i>D_x</i> = 1.986 Mg m ⁻³
Triclinic, <i>P</i> 1	Mo <i>K</i> α radiation
<i>a</i> = 9.257 (6) Å	Cell parameters from 21 reflections
<i>b</i> = 10.483 (2) Å	θ = 4.9–22.0°
<i>c</i> = 10.6838 (17) Å	μ = 6.51 mm ⁻¹
α = 103.807 (12)°	<i>T</i> = 298 (2) K
β = 92.84 (3)°	Irregular, yellow
γ = 103.09 (5)°	0.22 × 0.21 × 0.20 mm
<i>V</i> = 974.7 (7) Å ³	

Data collection

Bruker <i>P4</i> diffractometer	<i>R</i> _{int} = 0.026
2 θ / ω scans	θ _{max} = 25°
Absorption correction: empirical via ψ scan (North <i>et al.</i> , 1968)	<i>h</i> = -10 → 1
<i>T</i> _{min} = 0.213, <i>T</i> _{max} = 0.272	<i>k</i> = -11 → 12
4089 measured reflections	<i>l</i> = -12 → 12
3399 independent reflections	3 standard reflections
3207 reflections with <i>I</i> > 2 σ (<i>I</i>)	every 97 reflections
	intensity decay: none

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)] = 0.033	$w = 1/[\sigma^2(F_o^2) + (0.08P)^2]$
<i>wR</i> (<i>F</i> ²) = 0.096	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 1.03	(Δ/σ) _{max} = 0.002
3399 reflections	$\Delta\rho$ _{max} = 1.57 e Å ⁻³
244 parameters	$\Delta\rho$ _{min} = -1.77 e Å ⁻³

Table 1

Selected geometric parameters (Å, °).

Re1—C3	1.888 (6)	Re1—N2	2.214 (5)
Re1—C2	1.922 (6)	Re1—Cl1	2.4685 (17)
Re1—C1	1.927 (8)	N3—O4	1.343 (9)
Re1—N1	2.208 (5)	N3—C4	1.345 (9)
C3—Re1—C2	87.1 (3)	C1—Re1—N2	95.6 (3)
C3—Re1—C1	87.9 (3)	N1—Re1—N2	80.27 (19)
C2—Re1—C1	90.4 (3)	C3—Re1—Cl1	178.04 (19)
C3—Re1—N1	93.0 (2)	O4—N3—C4	111.6 (7)
C1—Re1—N1	175.9 (2)		

Table 2

Hydrogen-bonding 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>
O4—H4...O5	0.82	1.88	2.681 (9)	164
C6—H6C...O3	0.96	2.51	3.369 (12)	150
C21—H21...O5 ⁱ	0.93	2.50	3.211 (9)	133

Symmetry code: (i) *x*, 1 + *y*, *z*.

H atoms were assigned by assuming idealized geometry, with C—H distances of 0.96 and 0.93 Å for the aliphatic and aromatic H atoms, respectively, and an O—H distance of 0.82 Å. In the final refinement, seven peaks with residual electron density greater than $1 \text{ e } \text{Å}^{-3}$ were observed. Six are ghosts of the Re atom and one is due to the non-bonding pair of electrons on atom N3 of the oxime moiety. The deepest hole was observed 0.91 Å from Re.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (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: FG1636). Services for accessing these data are described at the back of the journal.

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