

## The optical sensor *fac*-tricarbonyl-chloro(di-2-pyridylmethanone *p*-nitrophenylhydrazone)rhenium(I) dimethyl sulfoxide solvate

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

Received 25 April 2001

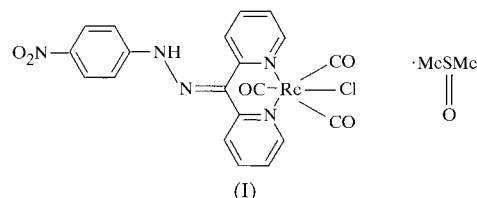
Accepted 21 August 2001

The first metal complex of di-2-pyridylmethanone *p*-nitrophenylhydrazone (dpknph), *i.e.* the title compound, *fac*-[ReCl(C<sub>17</sub>H<sub>13</sub>N<sub>5</sub>O<sub>2</sub>)(CO)<sub>3</sub>]·C<sub>2</sub>H<sub>6</sub>OS, crystallizes as well separated pseudo-tetrahedral DMSO (DMSO is dimethyl sulfoxide) and pseudo-octahedral *fac*-[ReCl(dpknph)(CO)<sub>3</sub>] moieties. Two N atoms from dpknph, three C atoms from the carbonyl groups and one chloride ion occupy the coordination sphere around rhenium. The coordinated dpknph ligand forms a six-membered ring in a boat conformation, with the pyridine rings in a butterfly formation. The *p*-nitrophenylhydrazone moiety is planar, with all C and N atoms in *sp*<sup>2</sup>-hybridized forms. The molecules pack as stacks of interlocked *fac*-[ReCl(dpknph)(CO)<sub>3</sub>]·DMSO units *via* a network of non-covalent bonds that include solute–solute, solvent–solute and  $\pi$ – $\pi$  interactions.

### Comment

The development of molecular systems sensitive to their surroundings is of interest because of their rich physico-chemical properties, reactivity patterns, and applications in devices employed in photonic, electronic and sensing techniques (Drain *et al.*, 2001; Luo *et al.*, 2001; Prasad & Williams, 1991; Bosshard *et al.*, 1995; Czerney & Grummt, 1997). The synthesis of di-2-pyridylmethanone *p*-nitrophenylhydrazone (dpknph) and its tricarbonylrhenium complex, *fac*-[ReCl(dpknph)(CO)<sub>3</sub>], have been reported (Bakir & Abdur-Rashid, 1999). Optical and thermodynamic measurements on *fac*-[ReCl(dpknph)(CO)<sub>3</sub>] in polar solvents have revealed strong solvent–solute and solute–solute interactions, and facile interconversion between two charge-transfer bands (Bakir *et al.*, 2000). Manipulation of the charge-transfer bands in *fac*-[ReCl(dpknph)(CO)<sub>3</sub>]·DMSO, (I), led to the use of these systems, *i.e.* *fac*-[ReCl(dpknph)(CO)<sub>3</sub>] and surrounding solvent molecules, as spectrophotometric sensors for a variety of substrates that include metal ions. The structure of (I) is reported here and compared with the structures of

tricarbonylrhenium compounds containing  $\alpha$ -diimine ligands, *e.g.* di-2-pyridyl ketone oxime (dpk-oxime) and hydroxydi(2-pyridyl)methoxide (dpkO,OH).



A displacement ellipsoid plot of (I) is shown in Fig. 1, and Table 1 contains selected bond distances and angles. Two N atoms of the bidentate chelating dpknph ligand and two carbonyl C atoms occupy the equatorial positions in *fac*-[ReCl(dpknph)(CO)<sub>3</sub>] and the two axial positions are occupied by a carbonyl C atom and a Cl atom. The *N,N*-chelating dpknph molecule forms a six-membered Re1–N1–C15–C–C25–N2 metalocyclic ring in a boat conformation. The N–Re–N bite angle of 83.32 (12)<sup>o</sup> is of the same order as those reported for tricarbonylrhenium compounds of *N,N*-bidentate polypyridyl-like ligands containing six-membered rings (Bakir, 2001; Gerber *et al.*, 1993, 1995). For example, an N–Re–N bite angle of 84.6 (4)<sup>o</sup> was reported for dpkO,OH in [ReOCl<sub>2</sub>(dpkO,OH)] (Gerber *et al.*, 1993, 1995) and a bite angle of 80.27 (19)<sup>o</sup> was observed for dpk-oxime in *fac*-[ReCl(dpknph)(CO)<sub>3</sub>]·DMSO (Bakir, 2001). The carbonyl groups are in facial positions, with an average C–Re–C bond angle of 89.4 (3)<sup>o</sup>. The Re–C, Re–N and Re–Cl bond distances are normal and similar to those reported for *fac*-[ReCl(dpknph)(CO)<sub>3</sub>]·DMSO (Bakir, 2001) and a variety of tricarbonylrhenium compounds of the type *fac*-[ReCl(L–L)(CO)<sub>3</sub>], where L–L is an  $\alpha$ -diimine ligand (Horn & Snow, 1980; Xue *et al.*, 1998; Yam *et al.*, 1995, 1998; Gibson *et al.*, 1998). For example, in *fac*-[ReCl('Bu<sub>2</sub>bpy)(CO)<sub>3</sub>], the Re–C, Re–N and Re–Cl bond distances are 1.935 (9)/1.935 (9)/1.896 (3), 2.169 (6)/2.170 (5) and 2.476 (2) Å, respectively (Yam *et al.*, 1995). The *p*-nitrophenylhydrazone moiety in (I) is planar, with all C and N atoms in *sp*<sup>2</sup>-hybridized forms.

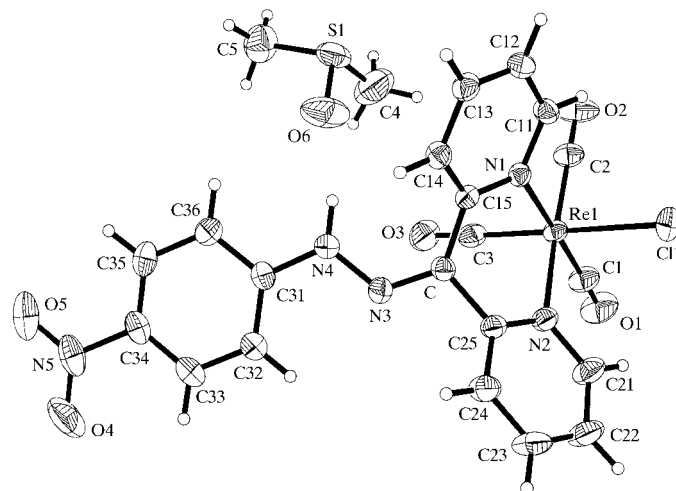
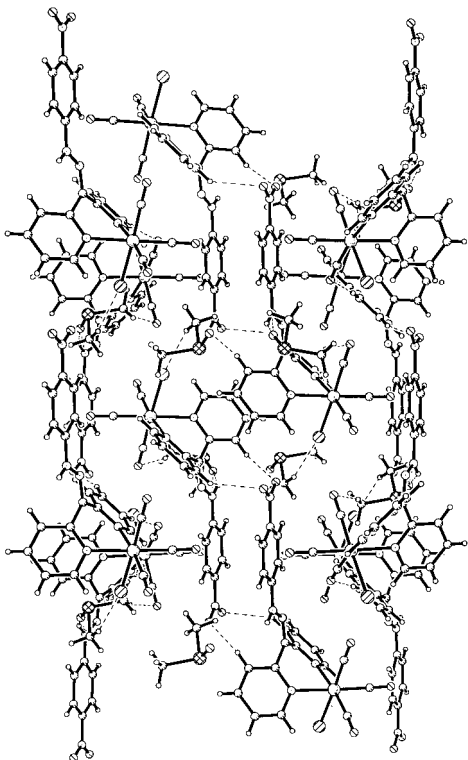


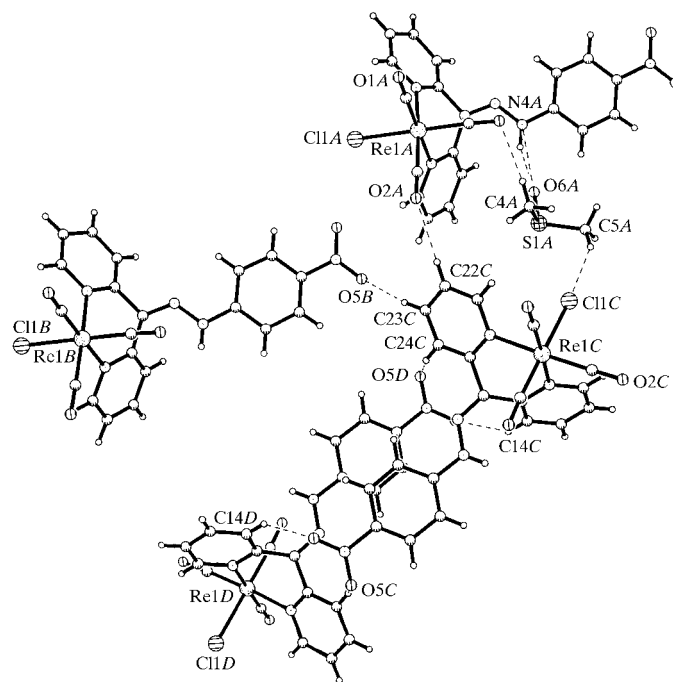
Figure 1

A view of the structure of (I), with displacement ellipsoids drawn at the 30% probability level.

The packing of molecules (Fig. 2) shows antiparallel stacks of (I), with the *p*-nitrophenylhydrazone (P-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-NH-N) moieties from adjacent stacks in a face-to-face orientation. The interplanar distance between the phenyl rings of approximately 3.45 Å is of the same order as the  $\pi$ -stacking distances in aromatic and charge-transfer compounds and is shorter than the interplanar distance of 4.97 Å reported for the pure benzene dimer (Glusker *et al.*, 1994; Batchelor *et al.*, 2000; Williams, 1993). The antiparallel arrangement of the *p*-nitrophenylhydrazone moieties facilitates the formation of intermolecular non-classical C—H...O hydrogen bonds between the nitro O4 and O5 atoms and the pyridine H14 and H24 atoms. A classical intramolecular N—H...O hydrogen bond, a non-classical intramolecular C—H...O hydrogen bond and a non-classical intermolecular C—H...Cl hydrogen bond were observed between DMSO and *fac*-[ReCl(dpknph)(CO)<sub>3</sub>] (Fig. 3). In addition, side-to-side intermolecular hydrogen bonds were observed between adjacent carbonyl groups, nitro groups and pyridine rings, *i.e.* C22—H22A...O2 and C23—H23A...O5. The bond distances and angles (Table 2) of the classical hydrogen bonds between the DMSO O6 atom and the amino N4—H4 group of the hydrazone moiety are similar to those reported for a variety of N—H...O hydrogen bonds (Bakir, 2001; Sherrington & Taskinen, 2001; Uppadine *et al.*, 2001; Glusker *et al.*, 1994; Pan *et al.*, 1997). For example, in 5-nitro-2-thiophenecarboxaldehyde 4-methylphenylhydrazone form I (NTMPH-I), two different N—H...O hydrogen bonds, with O—H = 2.0–2.3 Å, N—O = 3.01–3.18 Å and N—H...O = 161–160°, were observed (Pan *et al.*, 1997). The non-classical hydrogen bonds are of the same



**Figure 2**  
A view showing the packing of (I).



**Figure 3**  
A view showing classical and non-classical hydrogen bonds between DMSO and *fac*-[ReCl(dpknph)(CO)<sub>3</sub>] moieties. [Symmetry codes: (A)  $x, y, z$ ; (B)  $x, 2 - y, \frac{1}{2} + z$ ; (C)  $x, 1 - y, \frac{1}{2} + z$ ; (D)  $1 - x, 2 - y, 2 - z$ .]

order as the sum of their van der Waals radii; for example, the van der Waals O—H distance is about 2.8 Å (Glusker *et al.*, 1994; Pan *et al.*, 1997). The non-covalent interactions observed in this interlocking system (solute–solute and solvent–solute) may account for the optical and molecular-sensing behavior of (I), as any slight interaction between this system and its surroundings may disrupt the weak non-covalent interactions present. This is consistent with the low values of the activation parameters reported for the interconversion between the charge-transfer bands in *fac*-[ReCl(dpknph)(CO)<sub>3</sub>] (Bakir *et al.*, 2000) and the low values for the bond energies of non-covalent interactions (Vishweshwar *et al.*, 2001). The layer arrangement of (I) and the planar hydrazone moiety may also account for the observed fast electronic transfer in *fac*-[ReCl(dpknph)(CO)<sub>3</sub>] compared with dpknph (Bakir & Abdur-Rashid, 1999). Studies are in progress to grow single crystals of the uncoordinated dpknph molecule, with the aim of comparing its structure with the structure of (I).

In conclusion, structural studies of (I) revealed the presence of weak non-covalent interactions that include solvent–solute, solute–solute and  $\pi$ -stacking interactions, and which may account for the interlocked charge-transfer bands and molecular sensitivity of *fac*-[ReCl(dpknph)(CO)<sub>3</sub>] in polar solvents.

## Experimental

*fac*-[ReCl(dpknph)(CO)<sub>3</sub>] was synthesized as described previously (Bakir & Abdur-Rashid, 1999). Reagent grade DMSO used for the crystallization was thoroughly deoxygenated prior to use. When *fac*-

[ReCl(dpnph)(CO)<sub>3</sub>] was allowed to stand in DMSO for several days at room temperature, yellow–green crystals of (I) were obtained. A single crystal was selected and mounted on a glass fiber with epoxy cement and used for data collection.

#### Crystal data

[ReCl(C <sub>17</sub> H <sub>13</sub> N <sub>5</sub> O <sub>2</sub> )(CO) <sub>3</sub> ].C <sub>2</sub> H <sub>6</sub> OS	$D_x = 1.799 \text{ Mg m}^{-3}$
$M_r = 703.13$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 30 reflections
$a = 21.104 (2) \text{ \AA}$	$\theta = 10.7\text{--}22.4^\circ$
$b = 14.486 (2) \text{ \AA}$	$\mu = 4.91 \text{ mm}^{-1}$
$c = 18.962 (2) \text{ \AA}$	$T = 298 (2) \text{ K}$
$\beta = 116.408 (7)^\circ$	Irregular, yellow–green
$V = 5192.0 (10) \text{ \AA}^3$	$0.42 \times 0.38 \times 0.34 \text{ mm}$
$Z = 8$	

#### Data collection

Bruker P4 diffractometer	$R_{\text{int}} = 0.027$
$2\theta/\omega$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: $\psi$ scan (XSCANS; Bruker, 1996)	$h = -1 \rightarrow 25$
$T_{\text{min}} = 0.157$ , $T_{\text{max}} = 0.188$	$k = -1 \rightarrow 17$
5397 measured reflections	$l = -22 \rightarrow 20$
4562 independent reflections	3 standard reflections
3969 reflections with $I > 2\sigma(I)$	every 97 reflections
	intensity decay: none

#### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.026P)^2 + 8.0P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.064$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.37 \text{ e \AA}^{-3}$
4562 reflections	$\Delta\rho_{\text{min}} = -0.85 \text{ e \AA}^{-3}$
339 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Re1—Cl1	2.4654 (13)	N3—C	1.293 (5)
Re1—C1	1.900 (5)	N3—N4	1.345 (5)
Re1—C2	1.914 (5)	N4—C31	1.394 (6)
Re1—C3	1.902 (5)	N5—C34	1.458 (7)
Re1—N1	2.200 (3)	N5—O4	1.232 (7)
Re1—N2	2.193 (4)	N5—O5	1.220 (6)
C1—Re1—C2	90.3 (2)	C3—Re1—Cl1	177.63 (15)
C1—Re1—C3	88.8 (2)	N1—Re1—N2	83.32 (12)
C2—Re1—C3	89.2 (2)	C—N3—N4	122.0 (4)
C2—Re1—N1	92.06 (16)	N3—N4—C31	116.4 (4)
C2—Re1—N2	173.34 (17)	O4—N5—O5	124.0 (5)
C3—Re1—N2	95.75 (17)		

**Table 2**

Hydrogen-bonding and short-contact geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N4—H4 $\cdots$ O6	0.93 (5)	1.85 (5)	2.775 (5)	169 (4)
C4—H4C $\cdots$ O3	0.96	2.85	3.364 (8)	115
C5—H5C $\cdots$ Cl <sup>i</sup>	0.96	2.83	3.716 (7)	153
C14—H14A $\cdots$ O4 <sup>ii</sup>	0.93	2.55	3.353 (7)	145
C22—H22A $\cdots$ O2 <sup>iii</sup>	0.93	2.47	3.393 (6)	174
C23—H23A $\cdots$ O5 <sup>iv</sup>	0.93	2.54	3.436 (7)	163
C24—H24A $\cdots$ O5 <sup>ii</sup>	0.93	2.53	3.308 (7)	142

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

The H atom involved in the amine-to-solvent hydrogen bond was refined without constraints. All other H-atom positions were assigned by assuming idealized geometry, with C—H distances of 0.96 and 0.93  $\text{\AA}$  for aliphatic and aromatic H atoms, respectively. The DMSO molecule was slightly disordered such that the S atom existed in two different positions; the major orientation had an occupancy of 0.847 (4).

Data collection: XSCANS (Siemens, 1996); cell refinement: XSCANS; data reduction: SHELXTL (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

The author acknowledges The University of the West Indies, and the Inter-America Development Bank for funds to establish the X-ray laboratory at The University of the West Indies—Mona Campus.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1194). Services for accessing these data are described at the back of the journal.

## References

- Bakir, M. (2001). *Acta Cryst.* **C57**, 1154–1156.
- Bakir, M. & Abdur-Rashid, K. (1999). *Transition Met. Chem.* **24**, 384–388.
- Bakir, M., Abdur-Rashid, K. & Mulder, W. H. (2000). *Talanta*, **51**, 735–741.
- Batchelor, E., Klinowski, J. & Jones, W. (2000). *J. Mater. Chem.* **10**, 839–848.
- Bosshard, C., Sutter, K., Pretre, P., Hullinger, J., Florsheimer, M., Kaatz, P. & Gunter, P. (1995). *Organic Nonlinear Optical Materials*. Amsterdam: Gordon and Breach Science Publishers.
- Bruker (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
- Czerney, P. & Grummt, U. W. (1997). *Sensors Actuators Ser. B*, **38–39**, 395–400.
- Drain, C. M., Shi, X., Milic, T. & Nifatis, F. (2001). *J. Chem. Soc. Chem. Commun.* pp. 287–288.
- Gerber, T. I. A., Bruwer, J., Bandoli, G., Perils, J. & du Preez, J. G. H. (1995). *J. Chem. Soc. Dalton Trans.* pp. 2189–2192.
- Gerber, T. I. A., Kemp, H. J., du Preez, J. G. H. & Bandoli, G. (1993). *J. Coord. Chem.* **28**, 329–336.
- Gibson, D. H., Sleadd, B. A., Yin, X. & Vij, A. (1998). *Organometallics*, **17**, 2689–2689.
- Glusker, J. P., Lewis, J. P. M. & Rossi, M. (1994). *Crystal Structure Analysis for Chemists and Biologists*. New York: Wiley-VCH.
- Horn, E. & Snow, M. R. (1980). *Aust. J. Chem.* **33**, 2369–2376.
- Luo, J., Hua, J., Qin, J., Cheng, J., Shen, Y., Lu, Z., Wang, P. & Ye, C. (2001). *J. Chem. Soc. Chem. Commun.* pp. 171–172.
- Pan, F., Bosshard, C., Wong, M. S., Serbutoviez, C., Schenk, K., Gramlich, V. & Gunter, P. (1997). *Chem. Mater.* **9**, 1328–1334.
- Prasad, P. N. & Williams, D. J. (1991). *Introduction to Nonlinear Optical Effects in Molecules and Polymers*. Canada: John Wiley and Sons Inc.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Sherrington, D. C. & Taskinen, K. A. (2001). *Chem. Soc. Rev.* **30**, 83–93.
- Siemens (1996). *XSCANS*. Version 2.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Uppadine, L. H., Drew, M. G. B. & Beer, P. D. (2001). *J. Chem. Soc. Chem. Commun.* pp. 291–292.
- Vishweshwar, P., Nangia, A. & Lynch, V. M. (2001). *J. Chem. Soc. Chem. Commun.* pp. 179–180.
- Williams, J. H. (1993). *Acc. Chem. Res.* **26**, 593–598.
- Xue, W.-M., Chan, M. C.-W., Su, Z.-M., Cheung, K.-K., Liu, S.-T. & Che, C.-M. (1998). *Organometallics*, **17**, 1622–1630.
- Yam, V. W.-W., Lau, V. C.-Y. & Cheung, K.-K. (1995). *Organometallics*, **14**, 2749–2753.
- Yam, V. W.-W., Wang, K.-Z., Wang, C.-R., Yang, Y. & Cheung, K.-K. (1998). *Organometallics*, **17**, 2440–2446.