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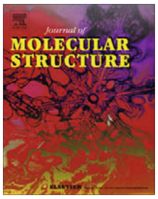

Synthesis, characterization and structure of the first rhenium compound of di-2-pyridyl ketone thiophene-2-carboxylic acid hydrazone (dpktah), *fac*-[Re(CO)$_3$(*N*,*N*-κ^2-dpktah)Cl]

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fac-[Re(CO)$_3$(κ^2-*N*,*N* -dpktah)Cl], isolated from the reaction between [Re(CO)$_5$Cl] and di-2-pyridyl ketone thiophene-2-carboxylic acid hydrazone (dpktah) in refluxing toluene, exhibits rich physico-chemical properties. The formulation of *fac*-[Re(CO)$_3$(κ^2-*N*,*N* -dpktah)Cl] was established from the results of its elemental analysis and spectroscopic measurements, and confirmed using X-ray crystallography. The ^{1}H NMR spectrum of *fac*-[Re(CO)$_3$(κ^2-*N*,*N*-dpktah)Cl] revealed the coordination of dpktah and exchange of the amide proton. Electronic absorption measurements show two intra-ligand charge transfer transitions (ILCT) and established inter-conversion between *fac*-[Re(CO)$_3$(κ^2-*N*,*N*-dpktah)Cl] and its conjugate base. Thermo-optical studies confirmed the facile inter-conversion between *fac*-[Re(CO)$_3$(κ^2-*N*,*N*-dpktah)Cl] and its conjugate base. Optosensing measurements show [MCl$_2$] (M = Zn, Cd or Hg) in concentrations as low as 1.00×10^{-7} M can be detected and determined using protophilic solutions of *fac*-[Re(CO)$_3$(κ^2-*N*,*N*-dpktah)Cl]. X-ray structural analysis done on a single crystal of *fac*-[Re(CO)$_3$(κ^2-*N*,*N*-dpktah)Cl] confirmed its identity and divulge two symmetry-independent molecules in the asymmetric unit. The supramolecular structure of *fac*-[Re(CO)$_3$(κ^2-*N*,*N*-dpktah)Cl] disclosed anti-parallel chains locked via a network of hydrogen bonds. Non-classic hydrogen bonds of the type C–H…Cl connect molecules in the chain and classic hydrogen bonds of the type N–H…O connect adjacent chains.

1. Introduction

Di-2-pyridyl ketone (dpk) and a range of its derivatives (see Scheme 1) are of current interest because of their physical properties, reactivity patterns, and applications in several areas [1–44]. We have been interested in the chemistry of di-2-pyridyl ketone derivatives and reported on the synthesis, structure, and electrochemical and spectroscopic properties of a variety of their compounds including *fac*-[M(CO)$_3$(κ^2-*N*,*N*-L-L)X] (M = Re or Mn; X = Cl or Br and L-L = dpk, dpkoxime and dpkhydrazone), *fac*-[Re(CO)$_3$(κ^3-*N*,*O*,*N*-dpkO,OH)], and [MCl$_2$(κ^3-*N*,*N*,*O*-dpkhydrazone)] (M = Zn or Cd) [7,12,35–44]. Spectroscopic measurements on dpk-hydrazones and their metal complexes in non-aqueous solvents show two intra-ligand charge transfer transitions (ILCT) that are sensitive to their surroundings [37,39,41,42,44]. Although there has been a growing interest in the chemistry of di-2-pyridyl ketone derivatives, the coordination chemistry of di-2-pyridyl ketone hydrazones is scarce and centered around the reactions between first-row metal salts and dpk-hydrazones to form complexes of the type [M(κ^3-*N*,*N*,*O*-dpkhydrazone)$_2$] for analytical or therapeutic applications [1–44]. In continuation of our efforts to exploit the coordination chemistry of dpk-derivatives, herein, we wish to report on the synthesis and characterization of the first rhenium compound of di-2-pyridyl ketone thiophene 2-carboxylic hydrazone (dpktah), *fac*-[Re(CO)$_3$(κ^2-*N*,*N*-dpktah)Cl], where dpktah binds to the metal center through the nitrogen atoms of its pyridyl groups. In previous reports we described the synthesis, characterization and structure of [CdCl$_2$(κ^3-*N*,*N*,*O*-dpktah)], where dpktah binds to cadmium using one nitrogen atom of its pyridyl group, a hydrazone nitrogen atom, and the carbonyl oxygen of the hydrazone backbone [12].

2. Experimental

2.1. Reagents and reaction procedures

The free ligand, dpktah, was prepared using a standard procedure as described for the synthesis of di-2-pyridyl ketone *p*-nitrophenyl hydrazone (dpknph) [37]. All other reagents were obtained from commercial sources and used without further purification.

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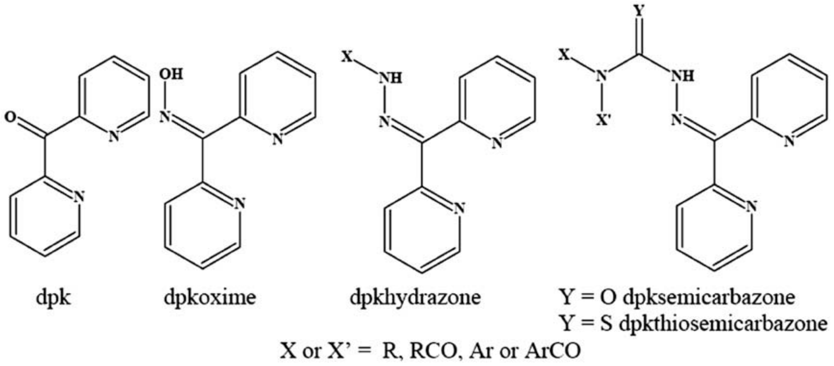


Scheme 1. Selected di-2-pyridyl ketone derivatives.

2.2. Preparation of *fac-[Re(κ^2-N,N-dpktah)(CO)$_3$Cl]*

A mixture of [Re(CO)$_5$Cl] (200 mg, 0.55 mmol), dpktah (0.22 mg, 0.70 mmol) and toluene (50 mLs) was refluxed for 20 h. The resulting reaction mixture was allowed to cool to room temperature and reduced in volume to ~25 mL. An off-yellow solid was filtered off, washed with hexane and diethyl ether, and dried; yield 230 mg (68%) (Found: C, 37.78; H, 2.18; N, 8.71. $C_{19}H_{12}ClN_4O_4SRe$ requires C, 37.16; H, 1.97; N, 9.12%). Infrared data (KBr disk, cm^{-1}): *v*(C≡O) 2020, 1910, 1873, *v*(C=O) 1644 and *v*(N–H) 3148 cm^{-1}. ^{1}H NMR (δ ppm): in dmso-d_6 12.06 (s, 0.8H, NH), 9.04 (d, 1H, dpk), 8.93 (d, 1H, dpk), 8.30 (t, 1H dpk), 8.23 (t, 1H, dpk), 8.9 (broad d, 1.4H, thiophene), 8.02 (d, 1H, dpk), 7.99 (d, 1H, dpk), 7.76 (t, 1H, dpk), 7.75 (t, 1H, dpk) and 7.25 (t, 1H, thiophene). UV–vis (CH_2Cl_2, nm): 326 (20,600.00); 287 (28,200.00); dmso: 440 (23,614.00), 324 (18,745.00); dmf: 440 (32,246.00), 324 (16,850.00).

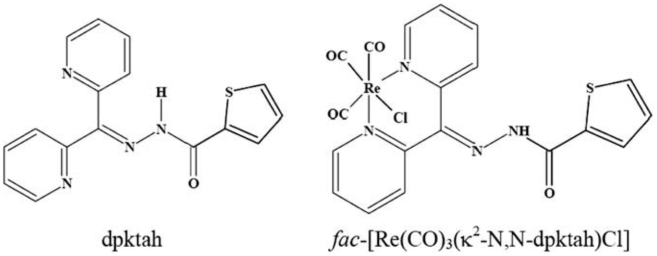
2.3. Physical measurements

Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 19 UV/VIS/NIR spectrometer. Solution 1H NMR spectra were recorded on a Bruker ACE 500 MHz Fourier-transform spectrometer and referenced to the residual protons in the incompletely deuterated solvent. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer Spectrum 1000 FT-IR Spectrometer.

Table 1
Crystal data and structure refinement for *fac*-[Re(CO)$_3$(κ2-*N*,*N*-dpktah)Cl]

Empirical formula	$C_{19}H_{12}ClN_4O_4ReS$
Formula weight	614.04
Temperature (K)	298(2) K
Wavelength (Å)	0.71073
Crystal system, space group	Triclinic, $P\bar{1}$
Unit cell dimensions	
a (Å)	10.854(4)
b (Å)	14.078(2)
c (Å)	14.3861(13)
α (°)	68.705(6)
β (°)	89.874(12)
γ (°)	89.70(2)
Volume (Å^3)	2048.1(8)
Z, calculated density (Mg/m^3)	4, 1.991
Absorption coefficient (mm^{-1})	6.200
F(000)	1176
Theta range for data collection (°)	2.41 to 19.99
Limiting indices	$-1 \leqslant h \leqslant 10$, $-12 \leqslant k \leqslant 12$, $-13 \leqslant l \leqslant 13$
Reflections collected/unique	4523/3740 [*R*(int) = 0.0269]
Completeness to θ = 19.99°	98.0%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3740/0/542
Goodness-of-fit on *F*^{2}	1.045
Final *R* indices [$I > 2\sigma(I)$][a,b]	$R_1 = 0.0444$, $wR_2 = 0.1184$
R indices (all data)	$R_1 = 0.0517$, $wR_2 = 0.1236$
Extinction coefficient	0.0016(3)
Largest diff. peak and hole (e Å^3)	1.787 and −1.254

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum w(F_o^2)^2]\}^{1/2}$; where $w = [\sigma^2(F_o^2) + (0.0957P)^2 + 1.84P]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$.



Scheme 2. dpktah and *fac*-[Re(CO)$_3$(κ^2-*N*,*N*-dpktah)Cl].

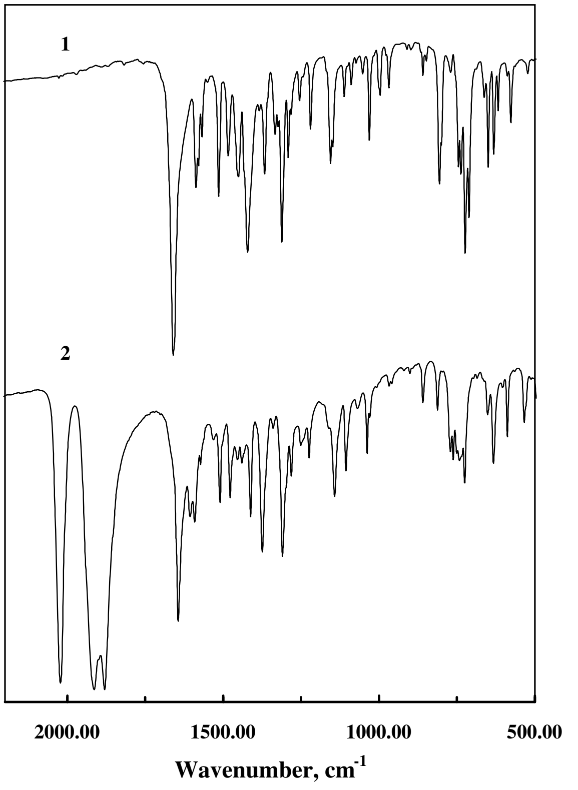


Fig. 1. Infrared spectra of dpktah (1) and *fac*-[Re(CO)$_3$(κ^2-*N*,*N*-dpktahCl] (2) measured in KBr.