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Molecular sensing behavior of the first Mn(I)-compound of di-2-pyridylketone-*p*-nitrophenylhydrazone (dpknph), *fac*-[Mn(CO)$_3$(dpknph)Br]

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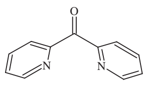
Abstract

The reaction between [Mn(CO)$_5$Br] and di-2-pyridylketone-*p*-nitrophenylhydrazone (dpknph) in diethyl ether under ultrasonic conditions gave *fac*-[Mn(CO)$_3$(dpknph)Br] in good yield. Optical and thermodynamic measurements on *fac*-[Mn(CO)$_3$(dpknph)Br] in non-aqueous polar solvents revealed reversible interconversion between two intense charge transfer absorption bands due to π–π^* (dpk), followed by dpk → nitro intraligand charge transfer transition (ILCT), mixed with metal ligand charge transfer transition (MLCT) due to $d\pi_{(\mathrm{Mn})} \rightarrow \pi^*_{(\mathrm{dpk})}$. In non-polar solvents, a single absorption band appeared. Extinction coefficients of 46200 ± 2000 and $28400 \pm 2000\ \mathrm{M^{-1}\,cm^{-1}}$ were calculated in DMSO for the low- and high-energy electronic states of *fac*-[Mn(CO)$_3$(dpknph)Br] using excess NaBF$_4$. Changes in enthalpy (ΔH°) of +14.0 and -12.1 kJ mol^{-1}, entropy (ΔS°) of +28.65 and -64.30 J mol^{-1} K^{-1}, and free energy (ΔG°) of +5.48 and +7.08 kJ mol^{-1} at 298 K were calculated for the interconversion between the high and low energy electronic states of *fac*-[Mn(CO)$_3$(dpknph)Br]. These results allow for the use of these systems (*fac*-[Mn(CO)$_3$(dpknph)Br] and surrounding solvent or solute molecules) as optical sensors for a variety of physical and chemical stimuli that include metal ions. Group 12 metal ions in concentrations as low as 1.00×10^{-9} M can be detected and determined using *fac*-[Mn(CO)$_3$(dpknph)Br] in dmso in the presence and absence of NaBH$_4$.

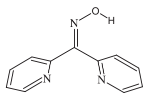
Keywords: Manganese; Carbonyl; Hydrazones; Sensors; Di-2-pyridyl ketone

1. Introduction

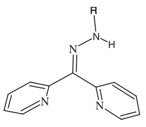
Manganese carbonyl compounds are of interest in part because of their rich physico-chemical properties, reactivity patterns and applications in many important chemical processes [1–10]. We have been interested in the chemistry of di-2-pyridyl ketone and its oxime and hydrazone derivatives (see below) and their metal compounds and reported on the synthesis and characterization of a variety of polypyridyl-like ligands and their metal compounds [11–25].



dpk



dpk.oxime



dpkhydrazone

The electrochemical behavior of *fac*-[Re-(CO)$_3$-(dpk)Cl] in the presence and absence of different substrates that include CO$_2$ and Groups I and II metal ions shows high sensitivity to solvent and substrate concentration and the use of *fac*-Re(CO)$_3$(dpk)Cl as an electrochemical sensor for Groups I and II metal ions [17,18]. In the case of CO$_2$, electrochemical reactions at metal and ligand sites of *fac*-Re(CO)$_3$(dpk)Cl were envisaged and

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the electrochemical response of *fac*-Re-$(CO)_3$ (dpk)Cl in the presence of metal ions depends on the polarizing power of the cation, i.e., charge density of cation, and cations with a large charge to radius ratio show the highest perturbation [17,18,22]. Electrochemical measurements on *fac*-$Re(CO)_3$(dpk · oxime)Cl show the oxime moiety to act as an electron sink/reservoir and its first reduction potential dpk · oxime/dpk · $oxime^{\bullet -}$ in non-aqueous media is solvent dependent and controlled by the proton-accepting ability of the solvent [19]. Plausible mechanisms for the reduction and oxidation of *fac*-Re-$(CO)_3$(dpk · oxime)Cl to *fac*-$Re(CO)_3$(dpkH · NH_2)Cl and *fac*-$Re(CO)_3$(dpk)Cl were proposed and consistent with the observed electrochemical transformations [19]. Spectroscopic and electrochemical measurements on solutions of *fac*-$Re(CO)_3$(dpknph)Cl and free dpknph show the metal complex to undergo faster electron transfer than the free ligand and the use of *fac*-Re- $(CO)_3$(dpknph)Cl as an optical sensor for metal ions [20,21]. X-ray crystallographic analysis on rhenium compounds of di-2-pyridyl ketone hydrazones revealed the presence of a web of non-covalent interactions that include solvent–solute and solute–solute interactions [11,14,15,24]. In a recent report, we described the synthesis and electrochemical behavior of manganese tricarbonyl compounds of *N*,*N*-bidentate di-2-pyridylketone (dpk), *fac*-[$Mn(CO)_3$- (dpk)Br] and its *N*,*O*,*N*-tridentate hydroxybis(2-pyridyl)methanolato anion (dpkO,OH^-), *fac*-[$Mn(CO)_3$- (dpk,O,OH))], and here we report on the synthesis and optosensing behavior of the first manganese compound of di-2-pyridyl ketone-4-nitrophenylhydrazone (dpkn-ph), *fac*-[$Mn(CO)_3$ (dpknph)-Br] [12].

2. Experimental

2.1. Reagents and reaction procedures

Solvents were of reagent grade and thoroughly deoxygenated prior to use. The compound dpknph was prepared as described previously [20]. All other reagents were obtained from commercial sources and used without further purification.

2.2. Preparation of *fac*-[$Mn(CO)_3$(dpknph)Br]

A mixture of $Mn(CO)_5Br$ (200 mg, 0.41 mmol), dpknph (200 mg, 0.60 mmol) and diethyl ether (100 mL) was allowed to stand in an ultrasonic bath for 0.5 h. The resulting orange precipitate was filtered off, washed with hexane, diethyl ether and dried; yield 150 mg (56%). *Anal.* Calc. for $C_{20}H_{13}BrN_5O_5Mn$: C, 44.63; H, 2.43; N, 13.00. Found: C, 44.75; H, 2.73; N, 12.88%. IR (KBr disk): ν(NH) 3200, ν(C$\equiv$O 2027 s, 1949 s and 1922 s $\nu(NO_2)$ st as 1599, $\nu(NO_2)$ st sy 1334 and $\nu(NO_2)$ γ 760 cm^{-1}.

2.3. Physical measurements

Electronic absorption spectra were recorded on a Perkin–Elmer Lambda 19 UV/VIS/NIR spectrometer or HP-8452A spectrophotometer. Infrared spectra were recorded as KBr pellets on a Perkin–Elmer Spectrum 1000 FT-IR Spectrometer. A Lauda-Brinkmann RM6 Circular Bath was used for temperature control.

2.4. Optical sensing studies

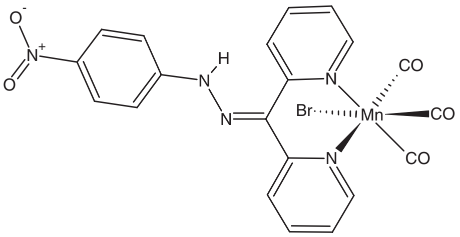
A stock solution of *fac*-[$Mn(CO)_3$(dpknph)Br] in DMSO and stock solutions of chemical stimulus ($NaBH_4$, $NaBF_4$ or Group 12 salts) in DMSO were prepared separately. Optical changes (electronic absorption spectral changes) were measured on a solution prepared by mixing appropriated volumes of *fac*-[$Mn(CO)_3$-(dpknph)Br] and stimulus solutions to prepare the desired solution (see figure captions for details). With the exception of the thermodynamic studies, all measurements were made at room temperature.

2.5. Analytical procedures

Elemental microanalyses were performed by MEDAC Ltd., Department of Chemistry, Brunel University, Uxbridge; UK.

3. Results and discussion

The first manganese compound of dpknph, *fac*-[$Mn(CO)_3$(dpknph)Br], was prepared in good yield from the reaction between [$Mn(CO)_5Br$] and dpknph in diethyl ether under ultrasonic conditions. This reaction is similar to those reported for the synthesis of *fac*-[$Mn(CO)_3$-(dpk)Br] from the reaction between [$Mn(CO)_5Br$] and dpk in diethyl ether under ultrasonic conditions [12]. The formulation of (**1**) as *fac*-[$Mn(CO)_3$(dpknph)Br] was based on its elemental analysis and confirmed from its infrared spectrum that confirmed its facial geometry and coordination of dpknph (see Section 2).



***fac*-[$Mn(CO)_3$(dpknph)Br]**