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X-ray crystallographic, spectroscopic and molecular sensing properties of *fac*-tricarbonylchloro(di-2-pyridylketonebenzoylhydrazone)rhenium(I) dimethylformamide solvate

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Abstract

The molecular sensor *fac*-[Re(CO)₃(dpkbh)Cl]·DMF (1) where DMF = *N*,*N*-dimethyl formamide and dpkbh = di-2-pyridylketonebenzoylhydrazone crystallized in the acentric triclinic space group P1. Structural analysis shows two units of (1) with rhenium in distorted octahedral geometry, the carbonyl groups are in facial positions with an average C–Re–C angle of 90° and the *N*,*N*bidentate dpkbh forms six-membered metallocyclic ring with rhenium in a boat conformation. The molecular packing shows the binding of DMF to *fac*-[Re(CO)₃(dpkbh)Cl] and helical strands of (1) interlocked via a network of hydrogen bonds. Optical measurements on *fac*-[Re(CO)₃(dpkbh)Cl] in DMF show the presence of two interlocked charge transfer bands at 440 and 318 nm that are highly sensitive to slight variations in their surroundings. As the concentration decreases, the intensity of the low energy absorption band at 440 nm increases and the reverse is observed when the concentration increases. Thermo-optical measurements on *fac*-[Re(CO)₃(dpkbh)Cl] in DMF established the reversible interconversion between the high and low energy electronic states of *fac*-Re(CO)₃(dpkbh)Cl and changes in enthalpy (ΔH^{\emptyset}) of + 17.44 ± 0.40 kJmol⁻¹, entropy (ΔS^{\emptyset}) of + 37.45 ± 0.50 J mol⁻¹ and free energy (ΔG^{\emptyset}) of + 6.27 ± 0.30 kJ mol⁻¹ in DMF were calculated. Acids or bases in concentration as low as 1.0×10^{-9} M can be detected and determined using *fac*-[Re(CO)₃(dpkbh)Cl] in DMF. ¹H-NMR measurements on *fac*-[Re(CO)₃(dpkbh)Cl] in DMF in non-aqueous media reveal high sensitivity to solvent and temperature variations and points to strong solvent-complex interactions. The amide protons and solvate protons show high sensitivity to temperature variations than the aromatic protons pointing to the participation of the amide proton in solvate-complex hydrogen bonds in non-aqueous solutions of *fac*-[Re(CO)₃(dpkbh)Cl].

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1. Introduction

The development of molecular systems sensitive to their surrounding has attracted a flurry of research activities in recent years for their use in part as sensitive reagents for the determination of trace amounts of biological and industrial substrates [1-7]. Bistability, i.e. the ability the systems (sensor plus surrounding molecules) to exist in two different states (electronic or

conformational) is important for molecular recognition as the interconversion between states allows to probe their structural relaxation and interactions with their surroundings [8]. The presence of organized non-covalent hydrogen bonds in materials was suggested by many authors to form polar chains and their appropriate packing may lead to the generation of acentric crystals required for non-linear optical responses, e.g. second harmonic generation [9,10]. We have been interested in the chemistry of di-2-pyridyl ketone (dpk) and its oxime and hydrazone derivatives (see below) because of their

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rich physico-chemical properties, reactivity patterns and applications in molecular recognition, catalysis and others [11-19].



In recent reports we described the synthesis of a series of di-2-pyridyl ketone hydrazones and reported on their optosensing behavior toward biomolecules and metal ions [17-22]. Metal ions in concentrations as low as 10^{-8} M can be detected and determined using di-2-pyridyl ketone hydrazones [19-21]. Structural studies on dpkbh (2), fac- $[Re(CO)_3(dpkbh)Cl]$ (3) where dpkbh = di-2-pyridylketonebenzoylhydrazone and fac-[Re(CO)3(dpkbh)Cl]·DMSO (4) where DMSO is dimethyl sulfoxide, revealed the presence of infinite one dimensional chains of non-coplanar pyridine rings in dpkbh, and centric and acentric units of (3) and (4), respectively [21-23]. The isolation of solvent free and DMSO solvated crystals of (3) confirms the high sensitivity of (3) to its surrounding and here the structure of DMF solvated fac-[Re(CO)₃(dpkbh)Cl] along with its solution optosensing and proton nuclear magnetic resonance properties are reported.

2. Experimental

2.1. Reagents

Solvents were reagent grade and thoroughly deoxygenated prior to use. All other reagents were obtained from commercial sources and used without further purification. *fac*-[Re(CO)₃(dpkbh)Cl] was prepared from the reaction between Re(CO)₅Cl and dpkbh in refluxing toluene as described in the literature [23]. Crystals of *fac*-[Re(CO)₃(dpkbh)Cl]·DMF were obtained from a DMF solution of *fac*-[Re(CO)₃(dpkbh)Cl] when allowed to stand at room temperature for several days.

2.2. X-ray crystallography

A single crystal isolated from a DMF solution of *fac*-[Re(CO)₃(dpkbh)Cl] was selected and mounted on a glass fiber with epoxy cement. A Bruker AXS with a Mo K α radiation and a graphite monochromator was used for data collection and the SHELXTL software package version 5.1 was used for structure solution [24,25]. Cell parameters and other crystallographic information are given in Table 1

Empirical formula C24H21CIN5O5Re Formula weight 681.11 Temperature 298(2) K Wavelength 0.71073 Å Crystal system, space group Triclinic, P1 Unit cell dimensions $a = 9.1300(10) \text{ Å} \alpha = 80.685(7)^{\circ}$ $b = 12.1673(11) \text{ Å } \beta = 81.978(10)^{\circ}$ $c = 12.4555(15) \text{ Å } \gamma = 75.235(7)^{\circ}$ Volume 1313.3(2) Å³ 2, 1.722 mg/m³ Z, Calculated density Absorption coefficient 4.771 mm⁻ F(000) 664 Crystal size $0.6 \times 0.8 \times 0.7 \text{ mm}^3$ Theta range for data collection $2.25 - 25.00^{\circ}$ Limiting indices $-10 \le h \le 1, -14 \le k \le 14,$ $-14 \le l \le 14$ Reflections collected/unique 5545/5545 [R(int) = 0.0000]Completeness to theta = 25.0099.6% Absorption correction Empirical 0.3873 and 0.3135 Max. and min. transmission Full-matrix least-squares on F^2 Refinement method Data/restraints/parameters 5545/7/651 Goodness-of-fit on F^2 1.011 Final *R* indices [I > 2sigma(I)]R1 = 0.0231, wR2 = 0.0691*R* indices (all data) R1 = 0.0236, wR2 = 0.0697Absolute structure parameter 0.106(12)0.0034(4) Extinction coefficient Largest diff. peak and hole 0.923 and $-0.901 \text{ e}\text{\AA}^{-3}$

along with additional details concerning data collection. All non-hydrogen atoms were refined with anisotropic thermal parameters.

2.3. Optical sensing studies

A stock solution of fac-[Re(CO)₃(dpkbh)Cl]·DMF in DMF and stock solutions of stimulus (NaOH, NaBH₄, NaBF₄ or citric acid) in DMF were prepared separately. Optical changes (electronic absorption spectral changes) were measured on solutions of fac-[Re(CO)₃(dpkbh)Cl] in the absence and presence of stimulus solutions in DMF (see figure captions for details). With the exception of thermooptical measurements, all measurements were made at room temperature.

2.4. Physical measurements

Electronic absorption spectra were recorded on a HP-8452A spectrophotometer or a Perkin–Elmer UV/VIS/NIR spectrometer λ -19. Baseline corrections on blank solvents were recorded prior to measurements. A Lauda-Brinkmann RM6 circular bath was used for temperature control. Solution ¹H NMR spectra were recorded on a Bruker AVANCE 500-MHz Fourier-transform spectrometer and referenced to the residual protons in the incompletely deuteriated solvent.

Table 1

Crystal data and structure refinement for fac-[Re(CO)3(dpkbh)Cl]·DMF

3. Results and discussion

3.1. Structural studies

A view of the molecular structure of fac-[Re(CO)3(dpkbh)Cl]DMF is shown in Fig. 1 and selected bond distances and angles are given in Table 2. Two well separated units of fac-[Re(CO)₃(dpkbh)Cl]·DMF were observed with two nitrogen atoms from the pyridyl rings, three carbon atoms from the carbonyl groups, and one chloride atom occupying the pseudo octahedral coordinated sites of rhenium atoms. The N-N bidentate dpkbh forms a six membered metallocyclic ring with rhenium in a boat conformation and the pyridine rings in a butterfly (Λ) formation. This is similar to that reported for a variety of N,N-bidentate binding of di-2-pyridyl ketone and its oxime and hydrazone derivatives of rhenium tricarbonyl moiety [17,18,23]. The bond distances and angles are normal and similar to those reported for (2), (3), (4) and other related compounds although slight variations were noted, especially those related to the hydrazone backbone (C=N-NH-CO) (see Table 2) [23]. The amide (NH) and the acyl (CO) moiety are in anti conformation with torsional angles of 175.8 and -178.9° for H4-N4-C5-O4 and H4'-N4'-C5'-O4', respectively. These angles are of similar order as the 175.9 and 173.0° observed for the same angles in (4) and are significantly different than the -15.8 and 13.4° observed in (3). These results reveal that the anti-conformation is favored in hydrogen bonding solvent and the syn-conformation is favored in solvent free crystals. These results are consistent with the spectroscopic and electrochemical behavior of these systems in non-aqueous media where two interlocked electronic states were observed in hydrogen bonding solvents and a single electronic state was observed in non-coordinating solvents [23]. Thus it is

possible to assign the high energy electronic state of fac-[Re(CO)₃(dpkbh)Cl]·DMF in non-polar solvents (310 nm in CH₂Cl₂) to the syn-conformation and the low energy electronic state in hydrogen binding solvent (440 nm in DMF) to the anti-conformation. Although the hydrazone (C=N-NH-CO) moiety is semi-planar, the total hydrazone backbone (C=N-NH-CO-Ph) is not planar and is similar to those reported for (3) and (4).

The packing of molecules (Fig. 2) shows stacks of (1) interlocked via a network of hydrogen bonds (Table 3). This confirms the strong solvate-complex and complex-complex interactions in the solid state. The bond distances and angles of the hydrogen-bonds are of the same order as those observed in (4), *fac*-[Re(CO)₃(dpkphh)Cl]·CH₃CN and other related compounds [17,18,23]. For example, hydrogen-bond parameters of 1.98, 2.78 and 154.52; and 2.20, 3.00 and 156.02 were reported for $d_{(H \cdots A)}$, $D_{(D \cdots A)}$ and \angle DHA were reported for the N–H···O hydrogen bonds in (4) [23].

3.2. Spectroscopic properties

In previous reports we described the electronic absorption properties of dpkbh and *fac*-[Re(CO)₃(dpkbh)Cl] in non-aqueous solvents and revealed the presence of bistable charge transfer absorption bands [21,23]. For the free uncoordinated dpkbh, these bands are intra-ligand charge transfer (ILCT) assigned to dpk π to π^* transition followed by dpk to benzoyl charge transfer. In the case of *fac*-[Re(CO)₃(dpkbh)Cl], although these transitions are ligand dominated, the high energy electronic transition may be mixed with a MLCT transition due to d_{π}(Re) to π^* (dpk) as a variety of Re(I)-carbonyl compounds of the type *fac*-[Re(CO)₃(L-L)Cl], where L-L = α -dimine ligand, have their MLCT band reported in the same vicinity observed for



Fig. 1. The molecular structure of *fac*-[Re(CO)₃(dpkbh)Cl]·DMF. The thermal ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Table 2 Bond lengths (Å) and angles (°) for fac-[Re(CO)₃(dpkbh)Cl], fac-[Re(CO)₃(dpkbh)Cl]·DMSO and fac-[Re(CO)₃(dpkbh)Cl]·DMF

	<i>fac</i> -[Re(CO) ₃ (dpkbh)Cl]	<i>fac</i> -[Re(CO) ₃ (dpkbh)Cl]·DMSO	<i>fac</i> -[Re(CO) ₃ (dpkbh)Cl]·DMF
Bond distances			
Re(1) - C(1)	1.901(11)	1.93(2)	1.832(13)
Re(1) - C(2)	1.909(10)	1.926(14)	1.928(12)
Re(1) - C(3)	1.900(18)	1.904(9)	1.938(18)
Re(1) - N(1)	2.209(7)	2.20(2)	2.220(12)
Re(1) - N(2)	2.189(7)	2.154(19)	2.308(13)
Re(1)-Cl(1)	2.457(4)	2.485(7)	2.468(5)
Re(1') - C(1')	1.938(15)	1.93(3)	2.025(14)
Re(1') - C(2')	1.930(18)	1.910(9)	1.83(2)
Re(1') - C(3')	1.946(9)	1.910(9)	1.848(18)
Re(1') - N(1')	2.221(10)	2.210(15)	2.177(15)
Re(1') - N(2')	2.149(11)	2.242(18)	2.084(12)
Re(1') - Cl(1')	2.455(2)	2.459(7)	2.482(4)
N(3) - C(4)	1.258(16)	1.21(3)	1.287(19)
N(3) - N(4)	1.374(11)	1.41(2)	1.354(15)
N(4) - C(5)	1.37(2)	1.47(3)	1.348(19)
C(5) - O(4)	1.230(15)	1.14(3)	1.151(16)
N(3') - C(4')	1.283(11)	1.33(2)	1.296(14)
N(3') - N(4')	1.368(10)	1.29(3)	1.357(13)
N(4') - C(5')	1.347(15)	1.38(4)	1.43(2)
C(5') - O(4')	1.236(14)	1.29(3)	1.24(2)
Bond angles			
C(3) - Re(1) - C(1)	90.2(6)	91.9(10)	91.1(6)
C(1) - Re(1) - C(2)	87.8(4)	91.9(9)	87.6(6)
C(3) - Re(1) - N(2)	91.6(4)	92.1(9)	90.7(5)
C(1) - Re(1) - N(2)	95.9(4)	92.8(8)	97.8(5)
C(2) - Re(1) - N(2)	176.2(3)	173.8(8)	174.5(6)
C(3)-Re(1)-N(1)	93.1(4)	94.4(10)	95.4(5)
N(2)-Re(1)-N(1)	83.4(3)	81.7(8)	82.0(4)
C(3) - Re(1) - Cl(1)	175.5(3)	177.1(9)	174.1(5)
N(1) - Re(1) - Cl(1)	84.3(3)	83.2(6)	80.2(3)
C(2')-Re(1')-C(1')	87.8(7)	85.8(10)	90.2(8)
C(1')-Re(1')-C(3')	90.1(5)	87.2(11)	80.9(7)
C(2')-Re(1')-N(2')	176.1(4)	173.7(7)	173.3(9)
C(1')-Re(1')-N(2')	95.6(6)	92.4(10)	93.4(5)
C(3')-Re(1')-N(2')	92.5(4)	93.8(10)	95.8(6)
C(2')-Re(1')-N(1')	93.0(5)	97.7(7)	
C(1')-Re(1')-N(1')	176.6(3)	176.5(11)	174.8(6)
C(3')-Re(1')-N(1')	93.1(4)	93.2(9)	94.4(7)
N(2')-Re(1')-N(1')	83.5(4)	84.0(6)	85.0(5)
C(3') - Re(1') - Cl(1')	175.8(4)	175.9(10)	178.0(6)
N(1')-Re(1')-Cl(1')	84.32(19)	85.8(4)	87.6(3)
C(4) - N(3) - N(4)	121.4(10)	116.1(19)	115.2(11)
N(3)-N(4)-C(5)	121.0(10)	110.2(15)	116.6(11)
O(4) - C(5) - N(4)	118.2(13)	127.6(19)	126(3)
N(4')-N(3')-C(4')	120.7(7)	117.2(16)	120.4(9)
N(3')-N(4')-C(5')	120.4(8)	123.1(18)	118.6(10)
O(4') - C(5') - N(4')	120.0(11)	115(2)	100.1(19)

the high energy ILCT band [21,23]. Manipulation of the equilibrium distribution of the electronic states allowed calculations of the extinction coefficients of dpkbh and *fac*-[Re(CO)₃(dpkbh)Cl] in non-aqueous media by the addition of a substrate that pushes the equilibrium into one favorable electronic state. In DMF extinction coefficients of 45,000 \pm 2000 and 15,000 \pm 2000 M⁻¹ cm⁻¹ were

calculated for dpkbh at 392 and 324 nm, respectively in the presence and absence of NaOH or citric acid. For *fac*-[Re(CO)₃(dpkbh)Cl], extinction coefficients of 23,709 \pm 2000 and 22,450 \pm 2000 cm⁻¹ M⁻¹ were calculated at 440 and 318 nm, respectively, using NaBH₄ and NaBF₄ to push the electronic states to the low and high energy forms. Although we reported the optical properties of *fac*-[Re(CO)₃(dpkbh)Cl] in DMSO, here we report on the optical behavior of *fac*-[Re(CO)₃(dpkbh)Cl] in DMF [23].

The electronic absorption spectra of *fac*-[Re(CO)₃(dpkbh)Cl] is concentration dependent. As the concentration decreases, the low energy electronic state at 440 nm becomes favorable and the reverse is observed when the concentration of fac-[Re(CO)₃(dpkbh)Cl] increases. These results point to solvent-complex interactions and hint to reversible interconversion between the high and low energy electronic states of fac-[Re(CO)₃(dpkbh)Cl] in DMF. When the temperature was allowed to increase on a DMF solution of fac-[Re(CO)₃(dpkbh)Cl], the ratio of the absorbance of low energy to high energy electronic states increases and when the temperature was allowed to decrease, the reverse was observed. These results confirm the reversible interconversion between the low and high energy electronic states of fac-[Re(CO)₃(dpkbh)Cl] and allowed for calculations of the thermodynamic parameters for the interconversion between the high and low energy electronic states of fac-[Re(CO)3(dpkbh)Cl] in DMF. A plot of $\ln(A_{440}/A_{318})$ versus $1/T \times 10^3$, K⁻¹ (see Fig. 3) gave a straight line with a slope of -2.10 ± 0.32 per unit decade and an intercept of $+4.56 \pm 0.04$ that gave changes in enthalpy (ΔH^{\varnothing}) of +17.44 ± 0.40 kJ mol⁻¹, entropy (ΔS^{\varnothing}) of + 37.45 \pm 0.50 J mol⁻¹ and free energy (ΔG^{\varnothing}) of $+6.27 \pm 0.30 \text{ kJ mol}^{-1}$ in DMF.

For the following interconversion:

$$\beta - fac \cdot [\text{Re}(\text{CO})_3(\text{dpkbh})\text{Cl}]$$

$$\Rightarrow \alpha - fac \cdot [\text{Re}(\text{CO})_3(\text{dpkbh})\text{Cl}]$$
(1)

where β is the conformation at high energy (318 nm) and α is the conformation at low energy (440 nm)

Application of Beer's Law gives:

$$A_{\alpha}/A_{\beta} = \varepsilon_{\alpha}c_{\alpha}/\varepsilon_{\beta}c_{\beta} \tag{2}$$

and

$$\ln(A_{\alpha}/A_{\beta}) = \ln(\varepsilon_{\alpha}/\varepsilon_{\beta}) + \ln K$$
(3)

The equilibrium constant is related to the thermodynamic parameters as shown in Eq. (4):

$$\ln K = \Delta S^{\varnothing} / R - \Delta H^{\varnothing} / RT \tag{4}$$

and substitution of Eq. (4) into Eq. (3) gives:

$$\ln(A_{\alpha}/A_{\beta}) = \ln(\varepsilon_{\alpha}/\varepsilon_{\beta}) + \Delta S^{\varnothing}/R - \Delta H^{\varnothing}/RT$$
(5)

A plot of $\ln(A_{\alpha}/A_{\beta})$ versus 1/T gives a straight line with a gradient of $-\Delta H^{\varnothing}/R$ and an intercept of $\{\ln(\varepsilon_{\alpha}/\varepsilon_{\beta}) + \Delta S^{\varnothing}/R\}$.



Fig. 2. A view of the packing of *fac*-[Re(CO)₃(dpkbh)Cl]·DMF.

In DMSO changes in enthalpy (ΔH^{\varnothing}) of $+4.10 \pm 0.20$ kJ mol⁻¹, entropy (ΔS^{\varnothing}) of $+8.23 \pm 0.45$ J mol⁻¹ and free energy (ΔG^{\oslash}) of $+1.66 \pm 0.20$ kJ mol⁻¹ were reported [23]. These results reveal that the high to low energy electronic state conversion is more favorable in DMSO than DMF.

The electronic absorption spectra of fac-[Re(CO)₃(dpkbh)Cl] in DMF in the presence or absence of a stimuli are sensitive

Table 3 Hydrogen bonds for fac-[Re(CO)₃(dpkbh)Cl]·DMF (Å and °)

d(D-H)	$d(\mathbf{H} \cdot \cdot \cdot \mathbf{A})$	$d(\mathbf{D} \cdot \cdot \cdot \mathbf{A})$	∠(DHA)		
0.86	2.13	2.88	145.93		
0.86	2.05	2.81	147.11		
0.96	2.40	2.81	105.61		
0.96	2.57	3.37	141.66		
0.93	2.59	3.24	127.41		
0.93	2.43	3.08	126.88		
0.93	2.53	3.41	156.47		
0.93	2.88	3.62	145.30		
0.93	2.83	3.68	144.20		
	d(D-H) 0.86 0.96 0.93 0.93 0.93 0.93 0.93	$\begin{array}{c ccccc} 0.86 & 2.13 \\ \hline 0.86 & 2.05 \\ \hline 0.96 & 2.40 \\ 0.96 & 2.57 \\ 0.93 & 2.59 \\ 0.93 & 2.43 \\ 0.93 & 2.53 \\ 0.93 & 2.88 \\ 0.93 & 2.83 \\ \end{array}$	$d(D-H)$ $d(H\cdots A)$ $d(D\cdots A)$ 0.86 2.13 2.88 0.86 2.05 2.81 0.96 2.40 2.81 0.96 2.57 3.37 0.93 2.59 3.24 0.93 2.53 3.41 0.93 2.88 3.62 0.93 2.83 3.68		



Fig. 3. A plot of $\ln(A_{440}/A_{318})$ versus $1/T \times 10^3$, K⁻¹ of 1.5×10^{-5} M fac-[Re(CO)₃(dpkbh)Cl] in DMF.



Fig. 4. Electronic absorption spectra of a mixture of 2.50×10^{-5} M fac-[Re(CO)₃(dpkbh)Cl] and 1.00×10^{-3} M NaOH in DMF (1) in the presence 1.00×10^{-9} (2), 2.00×10^{-9} (3), 5.00×10^{-9} (4), 1.00×10^{-8} (5), 5.00×10^{-8} (6), 2.00×10^{-7} (7) and 1.00×10^{-6} (8) *M* citric acid in DMF.

to variations in acid or base concentration. Fig. 4 shows the electronic absorption spectra of a mixture of fac-[Re(CO)₃(dpkbh)Cl] and NaOH in DMF in the presence of increasing amounts of citric acid. Similar results were obtained in the absence of NaOH and in both cases citric acid in concentrations as low as 1.0×10^{-9} M can be detected and determined using fac-[Re(CO)₃(dpkbh)Cl] in DMF. In the presence of NaOH, the absorbance of the low energy electronic state of fac-[Re(CO)₃(dpkbh)Cl] increases compared to the absorbance in the absence of NaOH and hence increases the optical window that can be utilized for optosensing measurements and hence improves the accuracy and sensitivity of these systems. A plot of the absorbance of fac-[Re(CO)3(dpkbh)Cl] in DMF in the presence and absence of NaOH versus concentration of citric acid is shown in Fig. 5 and reveals that citric acid in concentrations as low as 1×10^{-9} M can be detected and determined using fac-[Re(CO)₃(dpkbh)Cl] in the presence and absence of NaOH. The reverse was done when excess acid was added to a DMF solution of fac-[Re(CO)₃(dpkbh)Cl] and the resulting solution was titrated with NaOH solution in DMF.

The ¹H-NMR spectra of fac-[Re(CO)₃(dpkbh)Cl] in different solvents are shown in Fig. 6. These spectra reveal high sensitivity to solvent variations as apparent from the chemical shift variations of the amide (N–H) signal between 13 and 9 ppm, aromatic signals between 10 and 7 ppm and the solvate protons <4 ppm. These results hint to strong solvate-complex interactions and



Fig. 5. A plot of A_{440} (1 and 3) and A_{318} (2 and 4) of 2.50×10^{-5} M *fac*-[Re(CO)₃(dpkbh)Cl] in DMF in the absence of NaOH (1 and 4) and in the presence of 1.00×10^{-3} M NaOH (2 and 3) versus concentration of citric acid.

possible use of this system (fac-[Re(CO)₃(dpkbh)Cl] and surrounding solvent molecules) as a magnetosensor for a variety of stimuli. The ¹H-NMR spectra of fac-[Re(CO)₃ (dpkbh)Cl] are sensitive to temperature variations and the spectra in d₆-DMSO and CDCl₃ measured at different temperatures are shown in Figs. 7 and 8. From these spectra it is apparent that the chemical shifts of the amide



Fig. 6. ¹H-NMR spectra of *fac*-[Re(CO)₃(dpkbh)Cl]-DMF measured in d_{6} -DMSO, d_{7} -DMF, CDCl₃ and d_{6} -ACETONE at 30 °C.



Fig. 7. ¹H-NMR spectra of *fac*-[Re(CO)₃(dpkbh)Cl] measured in d₆-DMSO at 30, 40, 50 and 60 °C.

and solvate protons are more sensitive to temperature variations than the chemical shifts of the aromatic protons. A plot of the chemical shift of the amide and solvate protons versus $1/T \times 10^3$, K^{-1} (see Figs. 9 and 10) gave straight lines that gave slopes of -0.64 ± 0.05 , -0.40 ± 0.04 , -0.60 ± 0.02 and 0.34 ± 0.05 for the amide protons (see Fig. 9) and -0.76 ± 0.05 , -0.72 ± 0.05 , -0.68 ± 0.02 and 0.28 ± 0.05 for the solvate protons (see Fig. 10) in DMF, DMSO, (CD₃)₂CO



Fig. 8. ¹H-NMR spectra of *fac*-[Re(CO)₃(dpkbh)Cl] measured in CDCl₃ at 30, 40, 50 and 60 $^{\circ}$ C.



Fig. 9. A plot of chemical shift (δ) of the amide proton of *fac*-[Re(CO)₃(dpkbh)Cl] in different solvents versus $1/T \times 10^3$, K⁻¹.

and CDCl₃. The higher is the slope, the more sensitive the proton to temperature variation and points to the shielding of proton through inter- or intra-molecular hydrogen bonds from its surroundings. These results reveal that the amide proton in DMF, DMSO and (CD₃)₂CO is more shielded from its surrounding through a classic hydrogen



Fig. 10. A plot of chemical shift (δ) of the solvent proton of *fac*-[Re(CO)₃(dpkbh)CI] in different solvents versus $1/T \times 10^3$, K⁻¹.

bond of the type $N-H\cdots O$ than in CDCl₃. The aromatic protons show low sensitivity to temperature variations and no hydrogen bond analysis was done in this study. These results confirm the solvate-complex interactions and are in accord with the optical and structural results obtained in this study.

Owing the convenient synthesis of polypyridyl-like ligands and their metal compounds coupled with their rich physico-chemical properties, together with our continued interest in the development of molecular sensors, the coordination chemistry and sensing behavior of polypyridyl-like ligands and their metal compounds toward a variety of stimuli, including biomolecules and metal ions remains under investigation in our laboratories.

4. Conclusion

X-ray structural studies of *fac*-[Re(CO)₃(dpkbh)Cl]·DMF have revealed helical strands of *fac*-[Re(CO)₃(dpkbh)Cl]·DMF and a network of hydrogen bonds that include solvate-complex and complex–complex interactions. The electronic absorption spectra of *fac*-[Re(CO)₃(dpkbh)Cl]·DMF are sensitive to slight variations in their surrounding and substrates in concentrations as low as 10^{-9} M can be detected and determined using *fac*-[Re(CO)₃(dpkbh)Cl] in DMF. ¹H-NMR measurements reveal high sensitivity of the amide and solvate protons to solvent and temperature variations, point to strong solvate-complex interactions and are in accord with the optical and structural studies reported in this study.

References

- C.v. Bültzingslőwen, A.K. McEvoy, C. McDonagh, B.D. MacCraith, Anal. Chim. Acta 480 (2003) 275.
- M.-a. Haga, T. Takasugi, A. Tomie, M. Ishizuya, T. Yamada, M.D. Hossain, M. MiyaoInoue, J. Chem. Soc., Dalton Trans. (2003) 2069.
 A.G. Philip, Coord. Chem. Rev. 240 (2003) 191.
- [4] C.W. Rogers, M.O. Wolf, Coord. Chem. Rev. 233–234 (2002) 341.
- [5] C.J. Ward, P. Patel, T.D. James, Org. Lett. (Communication) 4 (2002) 477.
- [6] K.-H. Wong, M.C.-W. Chan, C.-W. Che, Chem.—Eur. J. 5 (1999) 2845.
- [7] V.V. Vasilèv, S.M. Borisov, Sensors Actuators B: Chem. 82 (2002) 272.
- [8] O. Kahn, Chem. Br. (1999) 24.
- [9] J. Ellena, G. Punte, B.E. Rivero, J. Chem. Crystallogr. 26 (1996) 319.
- [10] M.C. Etter, Acc. Chem. Res. 23 (1990) 120.
- [11] H. Kumagai, M. Endo, M. Kondo, S. Kawata, S. Kitagawa, Coord. Chem. Rev. 237 (2003) 197.
- [12] V. Camel, Spectrochim. Acta Part B 58 (2003) 1177.
- [13] C.J. Milios, E. Kefalloniti, C.P. Raptopoulou, A. Terzis, R. Vicente, N. Lalioti, A. Escuer, S.P. Perlepes, Chem. Commun. (2003) 819.
- [14] M. Bakir, J.A.M. McKenzie, J. Chem. Soc. Dalton Trans. (1997) 3571.
- [15] M. Bakir, J. Electroanal. Chem. 466 (1999) 60.
- [16] M. Bakir, I. Hassan, O. Green, J. Mol. Struct. 657 (2003) 75.
- [17] M. Bakir, Eur. J. Inorg. Chem. (2002) 481.
- [18] M. Bakir, Inorg. Chim. Acta 332 (2002) 1.
- [19] M. Bakir, K. Abdur-Rashid, C. Gyles, Spectrochim. Acta Part A 59 (2003) 2123.
- [20] M. Bakir, C. Gyles, J. Mol. Struct. 649 (2003) 133.
- [21] M. Bakir, O. Brown, J. Mol. Struct. 609 (2002) 129.
- [22] M. Bakir, C. Gyles, Talanta 56 (2002) 1117.
- [23] M. Bakir, O. Brown, Inorg. Chim. Acta 353 (2003) 89.
- [24] Bruker-SHELXTL, Software Version 5.1. Bruker AXS, Inc., Madison, WI, USA, 1997.
- [25] G. M. Sheldrick, SHELX97 and SHELXL97, University of Göttingen, Germany, 1997.