

Available online at www.sciencedirect.com



Journal of MOLECULAR STRUCTURE

Journal of Molecular Structure 889 (2008) 35-44

www.elsevier.com/locate/molstruc

X-ray crystallographic and molecular sensing properties of $[ZnCl_2(\kappa^2-N,N'-dpknph)]$ (dpknph = di-2-pyridyl ketone-*p*-nitrophenyl hydrazone)

Mohammed Bakir^{a,*}, Rebecca R. Conry^b, Orville Green^a

^a Department of Chemistry, The University of the West Indies-Mona Campus, Kingston 7, Jamaica, West Indies ^b Department of Chemistry, Colby College, 5764 Mayflower Hill, Waterville, ME 04901-8857, USA

Received 10 December 2007; received in revised form 8 January 2008; accepted 9 January 2008 Available online 17 January 2008

Abstract

When ZnCl₂ was allowed to react with di-2-pyridyl ketone p-nitrophenylhydrazone (dpknph) in acetonitrile under reflux, $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ was isolated in good yield. The formulation of the isolated product was established from the results of its elemental analysis and a number of spectroscopic measurements. Single crystal X-ray structural analysis done on $[\text{ZnCl}_2(\kappa^2-N, N'-\text{dpknph})]$.dmf isolated from a dmf solution of $[\text{ZnCl}_2(\kappa^2-N, N'-\text{dpknph})]$ shows the pyridine N, N'-bidentate binding of dpknph and revealed a serpentine polymeric network of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$.dmf units locked via a web of hydrogen bonds. ¹H NMR spectra of [ZnCl₂(κ^2 -N, N'-dpknph)] measured in d_6 -dmso, d_7 -dmf and d_6 -acetone confirmed the coordination of dpknph and showed partial exchange of the amide proton with solvent protons in d_6 -acetone and that $[\text{ZnCl}_2(\kappa^2-N, N'-\text{dpknph})]$ is stable in dmso and dmf. ¹H NMR variable temperature studies confirmed the stability of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ in d_6 -dmso and d_7 -dmf and showed the presence of temperature-dependent shielded protons due to hydrogen bonding. The electronic absorption spectra of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ in non-aqueous media show a single solvent-dependent intra-ligand-charge transfer (ILCT) transition of the donor-acceptor type between 300 and 700 nm. Thermo-optical measurements in protophilic solvent (dmso or dmf) between 303.15 and 353.15 K show the stability of $[ZnCl_2(\kappa^2 - N, N' - dpknph)]$ at those temperatures. In the presence of a base, a new ILCT peak appeared at 580 \pm 2 nm in dmso, and the addition of an acid to a mixture of [ZnCl₂(κ^2 -N, N'-dpknph)] and a base showed the disappearance of the peak at 580 ± 2 nm and reappearance of the peak due to [ZnCl₂(κ^2 -N, N'-dpknph)]. These results established reversible inter-conversion between $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ and its conjugate base, and allow for the use of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ in dmso to measure and detect substrates in concentrations as low as 1.00×10^{-5} M. Thermo-optical measurements on a mixture of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ and NaBH₄ in dmso confirmed the reversible inter-conversion between $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ and its conjugate base, and gave changes in enthalpy of 43.32 kJ/mol and entropy of 138.87 JK⁻¹ mol⁻¹ at 298.15 K. © 2008 Elsevier B.V. All rights reserved.

Keywords: Synthesis; Di-2-pyridyl ketone p-nitrophenylhydrazone metal complexes; Sensors; Zinc; X-ray diffraction

1. Introduction

Di-2-pyridyl ketone (dpk) and a range of its derivatives that include oxime, hydrazone, semicarbazone, thiosemicarbazone (see Scheme 1) and their metal compounds continue to attract research activities because of their physical properties, reactivity patterns and potential applications in medicine, catalysis and molecular sensing, etc. [1–26]. The pharmacological activity of several hydrazone, semicarbazone and thiosemicarbazone derivatives of di-2-pyridyl ketone has been demonstrated and several reports appeared on the metal chelating behavior of di-2-pyridyl ketone hydrazones and

^{*} Corresponding author. Tel.: +1 876 935 8164; fax: +1 876 977 1835. *E-mail address:* mohammed.bakir@uwimona.edu.jm (M. Bakir).



Scheme 1. dpk and its oxime and hydrazone derivatives.

di-2-pyridyl ketone thiosemicarbazone [18-20]. Di-2-pyridyl ketone derivatives are employed in analytical chemisand spectrophotometric try for the extraction determination of metal ions in solution and a recent report showed copper in concentrations as low as 7.24×10^{-8} M in natural water can be detected and determined using di-2-pyridyl ketone benzoylhydrazone [21-26]. Although numerous metal compounds of tridentate N.N'. O-di-2-pyridyl ketone benzovl hydrazone derivatives have been reported only three reports appeared on the N,N'-bidentate coordination of di-2-pyridyl ketone benzoyl hydrazone (see Scheme 2) [27-37]. We have been interested in the chemistry of di-2-pyridyl ketone and its derivatives and reported on the synthesis, spectroscopic and electrochemical properties, and structure of a variety of their derivatives and metal compounds [11,22,34,36-48]. Optical measurements on dpknph and its rhenium and ruthenium complexes in protophilic solvents (dmso or dmf) show high sensitivity of dpknph and its metal complexes to changes in their surroundings [22,39–41]. In order to elucidate the molecular sensing behavior of di-2-pyridyl ketone hydrazones, we embarked on the synthesis of their MCl₂ compounds and explored their optosensing behavior. In recent reports, we described the synthesis and structure of ZnCl₂ compounds of di-2-pyridyl ketone benzoyl hydrazone and di-2-pyridyl ketone thionyl hydrazone as forming a five-coordinate zinc compounds of the type $[ZnCl_2(\kappa^3-N,N',O-dpkhydrazone)]$ and here, we report on the synthesis of the four coordinate ZnCl₂ compound of di-2-pyridyl ketone p-nitrophenyl hydrazone [47,48].



fac -[Re(CO)₃(κ^2 -N,N'-dpkbh)Cl] fac-[Re(CO)₃(κ^2 -N,N'-dpkbh)Br]

2. Experimental

2.1. Reagents

All reagents were obtained from commercial sources and used without further purification. The ligand dpknph was prepared following a standard literature procedure [40].

2.1.1. Preparation of $[\text{ZnCl}_2(\kappa^2-N, N'-\text{dpknph})]$

A mixture of ZnCl₂ (300 mg, 2.20 mmol), dpknph (772 mg, 1.32 mmol) and acetonitrile (100 mL) was allowed to reflux in air for 3 h. The resulting yellow precipitate was filtered off, washed with hexane, diethyl ether and dried; yield 620 mg (62%) (found: C, 44.36; H, 2.86; N, 15.20. C₁₇H₁₃Cl₂N₅O₂Zn requires C, 44.81; H, 2.88; N, 15.37%). Infrared data (KBr disk, cm⁻¹): v(NH) 3220, v(CH) 3097-2900, v(py) 1597, v(NO₂) asym 1557, v(NO₂) sym 1345 and $v(NO_2)\gamma$ 749 cm⁻¹. UV-vis { λ/nm , ($\epsilon/$ $cm^{-1} M^{-1}$ in the concentration range $2 \times$ $10^{-5}-2 \times 10^{-6}$ M: in dmf 397 (20,000 ± 100) and 324 (3485 ± 100) ; in dmso 397 $(14,323 \pm 100)$, 324 $(2880 \pm$ 100), 276 (2,850 \pm 100); CH₃CN 393 (1680 \pm 100), 355 (sh) 336 $(15,460 \pm 100)$, 290 (sh), 283 (sh), 270 $(12,960 \pm 100)$ and 235 (sh), 225 $(14,460 \pm 100)$; CH₂Cl₂ 396 (315 ± 100) , 358 (sh), 342 $(18,765 \pm 100)$, 290 (sh), 282 (sh) and 273 (12,977 \pm 100). ¹H NMR (δ ppm): in dmf-d7 at 30 °C 13.52 (s, 1H, NH), 9.04 (d, 1H), 8.76 (d, 1H), 8.41 (d, 2H), 8.34 (d, 1H), 8.20 (t, 1H), 8.18 (t, 1H), 7.89 (d, 1H) and 7.76 (d, 2H), 7.74 (t, 1H) and 7.64 (t, 1H). ¹H NMR (δ ppm): in dmso- d_6 at 30 °C 12.96 (NH, 1H), 8.84 (d, 1H), 8.56 (d, 1H), 8.20 (d, 2H), 8.08 (d, 1H), 7.98 (t, 1H), 7.96 (t, 1H), 7.58 (d, 1H), 7.56 (t, 1H), 7.50 (d, 2H) and 7.43 (t, 1H).

2.2. X-ray crystallography

A single crystal isolated from the filtrate of the reaction mixture was selected and mounted on a glass fiber with epoxy cement. A Bruker SMART APEX CCD area detector diffractometer 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 [49–51]. Cell parameters and other crystallographic information are given in Table 1, along with additional details concerning data collection. All nonhydrogen atoms were refined with anisotropic thermal parameters. The water and the amide N4 hydrogen atoms were located from Fourier difference maps and refined without constraints. All other H-atom positions were refined assuming idealized geometry, with C–H distance of 0.93 Å and N1–H1A distance of 0.86 Å.

2.3. Optical sensing studies

A stock solution of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ in a protophilic solvent, and stock solutions of a stimulus (NaBH₄, NaBF₄ or ZnCl₂) in a protophilic solvent were prepared

Scheme 2. Views of fac-[Re(CO)₃(κ^2 -N, N'-dpkbh)X].

Largest diff. peak and hole 0.362 and -0.217 eA^{-3} ^a $R_1 = R_1 = \sum ||F_o| - |F_{9M}|| / \sum |F_o|.$ ^b $wR_2 = \{\sum [w(F_o^2 - F_o^2)^2] / \sum w(F_o^2)^2]\}^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.0546P)^2 + 0.000P]$ and $P = (F_o^2 + 2F_{9M}^2)/3.$

0.002(8)

Crystal data and structure refinement for $[ZnCl_2(\kappa^2-N, N'-dpknph)].dmf$

528.69

296(2)

0.71073

C20H20Cl2N6O3Zn

Monoclinic, P21

a = 7.0183(4) Å

b = 8.4161(5) Å

1153 35(12)

1.04-28.24°

 $-25 \leq l \leq 25$

5184/1/295

2, 1.522

1.331

96.1%

1.084

540

c = 19.6681(12) Å

 $-8 \leq h \leq 9, -11 \leq k \leq 10,$

10376/5184 [*R*(int) = 0.0169]

 $R_1 = 0.0279, wR_2 = 0.0731$

 $R_1 = 0.0301, wR_2 = 0.0799$

Full-matrix least-squares on F^2

 $\alpha = 90^{\circ}$

 $\gamma = 90^{\circ}$

 $\beta = 96.8870(10)^{\circ}$

separately. Optical changes (electronic absorption spectral changes) were measured on solutions prepared by mixing appropriate volumes of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ and stimulus solutions to prepare the desired solutions (see figure captions for details). All measurements were made at room temperature.

2.4. Equipment

Table 1

Empirical formula

Formula weight

Temperature (K)

Wavelength (Å)

Volume (Å³)

Limiting indices

Refinement method

Goodness-of-fit on F^2

R indices (all data)

F(000)

Unit cell dimensions

Crystal system, space group

Z, Calculated density (mg/m^3)

Absorption coefficient (mm^{-1})

Theta range for data collection

Reflections collected/unique

Completeness to $\theta = 28.21$

Data/restraints/parameters

Final *R* indices $[I \ge 2\sigma(I)]^{a,b}$

Absolute structure parameter

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 ACE 500-MHz Fourier-transform spectrometer and referenced to the residual protons in the incompletely deuteriated solvent. 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.

2.5. Molecular orbitals calculations

Restricted Hartree-Fock (RHF) semi-empirical molecular orbital calculations (PM3) on the lowest electronic state were conducted on a Hyperchem molecular modeling program using default parameters on singlet and triplet states. A Polak-Ribiere energy minimized model using MM⁺ force field was used [52].

3. Results and discussion

The reaction between ZnCl₂ and dpknph in acetonitrile under reflux gave $[ZnCl_2(\kappa^2-N, N'-dpknph)]$. The identity of the isolated compound was elucidated from the results of its elemental analysis, a number of spectroscopic measurements and an X-ray structural analysis done on a crystal of its dimethyl foramide (dmf) solvate grown from a dmf solution of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$. The infrared spectrum of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ show the coordination of dpknph as evident from the appearance of peaks associated with NH, CH, NO2 and C=C and C=N stretchvibrations [53]. The ¹H NMR spectra of ing $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ measured in d_6 -dmso, d_7 -dmf and d_6 -acetone (see Fig. 1) confirmed the coordination of dpknph to ZnCl₂ and revealed the sensitivity of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ to solvents as apparent from the significant change in chemical shift of the NH proton and slight changes in the chemical shifts of its aromatic protons in different solvents. While partial exchange of the NH proton occurs in d_6 -acetone, as noted by the broad character of the NH peak and the relative integration of the NH peak at 10.97 ppm to one CH peak (1H of the pyridine ring at 8.94 ppm) that gave a ratio of 0.5:1.0, the spectra show no exchange of the hydrazone NH proton in d_6 -dmso or d_7 -dmf as integration of the NH proton to the CH proton of coordinated pyridine ring for the complex in these solvents gave a ratio of 1:1. Variable temperature measurements in *d*₆-dmso solution of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ (see Fig. 2) show the NH proton and water protons exhibit higher temperature sensitivity compared to the other protons in the molecule. Minor temperature dependence was noted for the C11 and C21 protons while the other protons do not show any temperature dependence. In d_7 -dmf, the NH proton, solvent protons, phenyl protons and C11 and C21 show greater temperature dependence than the other protons. In d_6 -acteone, the C12, C13, C22 and C23 protons show higher temperature sensitivity compared to the other protons. Temperature-dependent protons reflect shielding from solvent due to hydrogen bonding, while solvent-exposed protons show no temperature dependence. The results confirm the sensitivity of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ to its surroundings. Plots of chemical shifts (δ) of NH versus 1/T, K in d_6 dmso and d_7 -dmf gave straight lines with slopes of -405and -282 per unit decade showing the NH proton of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ to be more sensitive to temperature variations in d_6 -dmso than in d_7 -dmf.

The electronic absorption spectra of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ measured in dmso, dmf, CH₃CN and CH₂Cl₂ are shown in Fig. 3. These spectra show $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ exhibits solvatochromic behavior. Further, single absorption peaks appeared at 420 nm in dmso and dmf, 410 nm in CH₃CH and 396 nm in CH₂Cl₂. The electronic absorption transitions of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ are intra-ligand-charge transfer (ILCT) due mainly to $\pi \rightarrow \pi^*$ of dpk followed by

37



Fig. 1. ¹H NMR spectra of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ measured in d_6 -dmso (a), d_7 -dmf (b) and d_6 -acetone (c) at 30 °C.



Fig. 2. ¹H NMR spectra of [ZnCl₂(κ^2 -N, N'-dpknph)] measured in d_6 -dmso at 30 (a), 40 (b), 50 (c) and 60 (d) °C.



Fig. 3. The electronic absorption spectra of 1.00×10^{-5} M [ZnCl₂(κ^2 -N, N'-dpknph)] in dmso, dmf, CH₃CN and CH₂Cl₂.

dpk \rightarrow NO₂ charge transfer mixed with Cl_p \rightarrow dpknph charge transfer. Semi-empirical PM3 molecular calculations (see Fig. 4) confirmed the assigned electronic transitions and gave a HOMO \rightarrow LUMO energy gap of 3.53 eV (351 nm). A plot of the absorbance of [ZnCl₂(κ^2 -N, N'-dpknph)] versus concentration in dmso and dmf gave straight lines with a slope of 33,240 ± 200 for dmso and 33,560 ± 200 in dmf. These results hint to the stability of [ZnCl₂(κ^2 -N, N'-dpknph)] in dmso and dmf, and the absence of any other absorbing species under these conditions. These results are in contrast to those reported for the optical behavior of the free ligand (dpknph) and its rhenium and ruthenium complexes fac-Re(CO)₃(dpknph)Cl and [Ru(bipy)₂(dpknph)]Cl₂ in dmso and dmf, where two ILCT transitions appeared between 300 and 800 nm and plots of absorbance versus concentration showed non-linearity pointing to strong complex–solvent interactions [22,42]. A comparison of



Fig. 4. Semi-empirical energy level diagram of $[\text{ZnCl}_2(\kappa^2-N, N'-\text{dpknph})]$.

the electronic absorption properties of $[\text{ZnCl}_2(\kappa^2-N, N'-\text{dpknph})\text{Cl}_2]$ with those reported for $[\text{ZnCl}_2(\kappa^3-N,N',O-\text{dpktah})]$ show the latter to exhibit two absorption peaks at 406 and 330 nm in dmso and a single absorption peak at 405 nm in dmf [51]. The absorption peaks in spectra of $[\text{ZnCl}_2(\kappa^3-N,N',O-\text{dpktah})]$ were assigned to $[\text{ZnCl}_2(\kappa^3-N,N',O-\text{dpktah})]$ and its conjugate base. In dmf, complete proton transfer from $[\text{ZnCl}_2(\kappa^3-N,N',O-\text{dpktah})]$ to dmf takes place, and in dmso, partial proton transfer occurs as noted by the appearance of two absorption peaks in dmso and one absorption peak in dmf. In CHCl₃ and CH₂Cl₂, a single absorption peak was observed

in the high energy region in the spectra of $[ZnCl_2(\kappa^3-N,N',O-dpktah)]$ and $[ZnCl_2(\kappa^2-N,N'-dpknph)Cl_2]$, pointing to the absence of any solvent complex interaction.

When $[\text{ZnCl}_2(\kappa^2-N, N'-\text{dpknph})]$ was allowed to interact with stoichiometric amounts of NaBH₄ in dmso, a new absorption peak appeared at 580 ± 2 nm, and as the concentration of NaBH₄ increased, the intensity of the absorption peak at 420 ± 2 nm diminished, and the intensity of the absorption peak at 580 ± 2 nm increased (see Fig. 5). The reverse was observed when stoichiometric amounts of NaBF₄ were added to a mixture of $[\text{ZnCl}_2(\kappa^2-N, N'-\text{dpknph})]$ and NaBH₄ dissolved in dmso. Under our



Fig. 5. Electronic absorption spectra of $[\text{ZnCl}_2(\kappa^2 - N, N' - dpknph)]$ 1.00×10^{-5} M in dmso in the presence of (1) 0.00, (2) 1.00×10^{-4} , (3) 5.00×10^{-4} , (4) 1.00×10^{-3} , (5) 2.00×10^{-3} , (6) 3.00×10^{-3} , (7) 5.00×10^{-3} , (8) 1.00×10^{-2} , (9) 2.00×10^{-2} and (10) 3.00×10^{-2} M NaBH₄.



Scheme 3. The inter-conversion between [ZnCl₂(κ^2 -N,N'-dpknph)] and its conjugate base.



Fig. 6. A plot of absorbance of a mixture of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ $(1.00 \times 10_{-5} \text{ M})$ and $NaBH_4$ $(5.00 \times 10^{-3} \text{ M})$ in dmso versus concentration of glucose. Table 2



Fig. 7. The molecular structure of $[\text{ZnCl}_2(\kappa^2-N, N'-dpknph)]$. The thermal ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Bond lengths [A] and angles [°] for $ZnCl_2(\kappa^2 - N, N' - dpknph)$].dmf							
Bond lengths							
Zn-N(2)	2.0348(18)	Zn-N(1)	2.0621(19)				
Zn–Cl(1)	2.1752(7)	Zn-Cl(2)	2.2097(7)				
N(1)-C(11)	1.338(3)	N(1)-C(15)	1.349(3)				
N(2)-C(21)	1.338(3)	N(2)-C(25)	1.345(3)				
C(11)–C(12)	1.372(4)	C(12)-C(13)	1.387(5)				
C(15)–C(01)	1.487(3)	C(22)-C(21)	1.376(4)				
C(01)–N(3)	1.287(3)	N(3)–N(4)	1.350(3)				
N(4)–C(31)	1.377(3)	N(4)-H(4)	0.77(3)				
C(31)–C(32)	1.396(3)	C(34)–N(5)	1.458(3)				
N(5)–O(2)	1.210(4)	N(5)–O(1)	1.225(5)				
C(1)–O(3)	1.229(4)	C(1)–N(6)	1.316(3)				
C(3) - N(6)	1.455(4)	C(2)–N(6)	1.442(4)				
Bond angles							
N(2)-Zn-N(1)	89.97(7)	N(2)– Zn – $Cl(1)$	118.67(6)				
N(1)– Zn – $Cl(1)$	112.97(6)	N(2)-Zn-Cl(2)	105.68(5)				
N(1)– Zn – $Cl(2)$	105.32(5)	Cl(1)– Zn – $Cl(2)$	119.67(3)				
C(11)–N(1)–C(15)	119.4(2)	C(11)-N(1)-Zn	120.95(17)				
C(15)–N(1)–Zn	116.91(14)	C(21)-N(2)-C(25)	118.98(19)				
C(21)-N(2)-Zn	122.39(15)	C(25)-N(2)-Zn	118.57(14)				
N(1)-C(11)-C(12)	122.8(3)	C(11)-C(12)-C(13)	117.9(2)				
N(1)-C(15)-C(01)	118.01(17)	N(2)-C(25)-C(24)	121.1(2)				
N(2)-C(25)-C(01)	119.05(18)	N(2)-C(21)-C(22)	122.6(2)				
N(3)-C(01)-C(15)	114.48(18)	C(15)-C(01)-C(25)	121.04(18)				
C(01)–N(3)–N(4)	120.09(19)	N(3)-N(4)-C(31)	119.2(2)				
N(4)–C(31)–C(36)	122.0(2)	C(32)-C(31)-C(36)	120.0(2)				
O(2)–N(5)–O(1)	123.4(3)	O(1)-N(5)-C(34)	118.1(3)				
O(3)–C(1)–N(6)	124.5(3)	C(1)-N(6)-C(2)	121.4(3)				

.

conditions, NaBH₄ did not reduce the hydrazone backbone but instead acted as a base while NaBF4 dissolved in dmso behaved as strong acid. This was further confirmed when excess benzoic acid was added to a dmso solution of a mixture of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ and NaBH₄ and the peak at 580 ± 2 nm disappeared. These reactions hint to reversible inter-conversion between the $[ZnCl_2(\kappa^2-N,N'-dpknph)]$ and its conjugate base (see Scheme 3) when allowed to interact with NaBH₄ and NaBF₄ and are similar to those reported for the acid-base inter-conversion between the free ligand and its conjugate base in dmso and dmf. In the presence of excess NaBH₄, the absorption peak at 420 ± 2 nm disappeared and the absorption peak at 580 ± 2 nm reached its maximum intensity, giving the extinction coefficient of $53000 \pm 200 \text{ M}^{-1} \text{ cm}^{-1}$ for conjugate base in dmf and dmso. A residual absorption peak appeared at $400 \pm 2 \text{ nm}$ when excess NaBH₄ was added to a dmso solution of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$ and that may be assigned to $Cl_p \rightarrow dpknph \ CT$.

Thermo-optical measurements on a mixture of $[\text{ZnCl}_2(\kappa^2-N, N'-dpknph)]$ and NaBH₄ dissolved in dmso show the intensity of the absorption peak at 580 ± 2 nm

increased and the intensity of the absorption peak at 420 ± 2 to decreased as the temperature was increased. The reverse was observed when the temperature was allowed to decrease. These results confirm reversible inter-conversion between $[\text{ZnCl}_2(\kappa^2-N, N'-\text{dpknph})]$ and its conjugate base. In the absence of NaBH₄, a slight decrease and shift to high energy of the absorption peak at 420 nm was observed and no evidence was noted for the appearance of an absorption peak due to the conjugate base. A plot of $\ln(A_{580}/A_{420})$ versus $1/T \times 10^3$ of a mixture of $[\text{ZnCl}_2(\kappa^2-N, N'-\text{dpknph})]$ and NaBH₄ in dmso gave a

Table 3					
Hvdrogen	bonds for	$[ZnCl_2(\kappa^2-N, N'-dpknph)].dm$	ıf [Å	and	٥]

, e	2()	1 1 / 1	L 3	
D–HA	d(D–H)	d(HA)	$d(D{\dots}A)$	<(DHA)
N(4)–H(4)O(3)	0.77(3)	2.06(3)	2.815(3)	165(3)
$C(11)-H(11)Cl(2)^{1}$	0.93	2.81	3.490(3)	130.4
C(2)-H(2A)O(3)	0.96	2.40	2.773(4)	102.6
$C(24) - H(24) \dots O(1)^2$	0.93	2.56	3.423(3)	155.1
$C(21)-H(21)Cl(1)^3$	0.93	2.80	3.612(2)	146.9

Symmetry transformations used to generate equivalent atoms: ${}^{1}x + 1, y, z$; ${}^{2}-x + 1, y + 1/2, -z + 1$ and ${}^{3}-x + 2, y + 1/2, -z$.



Fig. 8. Packing of molecules of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$. Non-covalent hydrogen bonds are represented by dashed lines.



Fig. 9. Views of the hydrogen bonds in $[\text{ZnCl}_2(\kappa^2-N, N'-\text{dpknph})]$.

straight line with a slope of -5.21 per unit decade and an intercept of 17.17 that gave changes in enthalpy of 43.32 kJ/mol and entropy of 138.87 JK⁻¹ mol^{-1,1} The low values for the thermodynamic parameters hint to facile inter-conversion between [ZnCl₂(κ^2 -N, N'-dpknph)] and its conjugate base in the presence of NaBH₄, and possible use as molecular sensor. This was further illustrated when a mixture of [ZnCl₂(κ^2 -N, N'-dpknph)]and NaBH₄ in dmso

 $[\operatorname{ZnCl}_2(\kappa^2 - N - N' - dpknph)] \leftrightarrow [\operatorname{ZnCl}_2(\kappa^2 - N - N' - dpknph - 1)]$ (1)

Application of Beer's law gives:

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

where $\alpha = [\text{ZnCl}_2(\kappa^2 - N - N' - dpknph - 1)]$ and $\beta = [\text{ZnCl}_2(\kappa^2 - N - N' - dpknph)]$

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):

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

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

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

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

was allowed to interact with stoichiometric amounts of glucose, and showed a decrease in the intensity of the absorption peak at 580 \pm 2 nm and an increase in the intensity of the absorption band at 420 \pm 2 nm as the concentration of glucose increased. A plot of absorbance versus concentration of added glucose (see Fig. 6) shows glucose concentrations as low as 1×10^{-6} M can be detected and determined using a mixture of [ZnCl₂(κ^2 -N, N'-dpknph)] and NaBH₄ in dmso.

The solid state structure of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$. dmf was determined using a single crystal X-ray crystallography. A view of the molecular structure of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$.dmf is shown in Fig. 7 and selected bond angles and distances are given in Table 2. The coordination about zinc is pseudo-tetrahedral with two nitrogen atoms from the pyridine rings of dpknph molecule and two chlorine atoms occupying the coordination sites. The pyridine N,N'-chelating dpknph molecule forms a six-membered Zn-N1-C15-C01-C25-N2 metallocyclic ring in a boat conformation. Some or all of this distortion from tetrahedral geometry about zinc is due to the constraints associated with the pyridine N,N'-bite angle of 90° in this structure, which is significantly larger than those reported for other transition metal compounds that contain pyridine N,N'-bidentate dpk-derivatives [45-47]. The bond distances of the coordinated atoms and those of the coordinated dpknph molecule appear normal as they are similar to those reported for a variety of zinc compounds that contain such bonds.

The packing of molecules shows a serpentine polymeric network of $[ZnCl_2(\kappa^2-N, N'-dpknph)]$.dmf units linked via a network of hydrogen bonds (Fig. 8 and Table 3). Each molecule within the bulk of the network binds to four adjacent molecules using its chlorine atoms, oxygen atom (O1) of the nitro-group, and hydrogen atoms of C11 and C21. The dmf molecule binds to the NH proton of the hydrazone via a classic O...H–N hydrogen bond (see Fig. 9a), and the chlorine atoms and oxygen atom (O1) of the nitro-group for non-classic hydrogen bonds of the type C–H...X (X = Cl or X) with neighboring molecules (see Fig. 9b and c), thus linking all $[ZnCl_2(\kappa^2-N,$ N'-dpknph)].dmf molecules together. The bond distances and angles of the hydrogen bonds are normal and similar to those reported for other molecules containing such bonds.

4. Conclusion

The first zinc complex of dpknph has been isolated and structurally characterized. Spectroscopic measurements of [ZnCl₂(κ^2 -N, N'-dpknph)] in protophilic solvents disclose sensitivity to its surroundings and substrates in concentrations as low as 1×10^{-6} M can be detected and determined using a mixture of [ZnCl₂(κ^2 -N, N'-dpknph)] and NaBH₄ in dmso.

¹ For the acid–base inter-conversion between $[ZnCl_2(\kappa^2-N-N'-dpknph)]$ and its conjugate base $[ZnCl_2(\kappa^2-N-N'-dpknph-1)]$:

Acknowledgments

We wish to thank Ms. Toni Johnson for NMR measurements and The University of the West Indies for financial support.

References

- M. Toyama, M. Nakahara, N. Nagao, Bull. Chem. Soc. Jpn. 80 (2007) 937.
- [2] C. Papatriantafyllopoulou, C.P. Raptopoulou, A. Escuer, C.J. Milios, Inorg. Chim. Acta 360 (2007) 61.
- [3] Z. Chen, F. Liang, S. Zhou, C. Xia, R. Hu, J. Mol. Struct. 827 (2007) 20.
- [4] D.-H. Lee, M.N. Murthy, K.D. Karlin, Bull. Chem. Soc. Jpn. 80 (2007) 732.
- [5] A. Grirrane, A. Pastor, E. Alvarez, C. Mealli, A. Ienco, P. Rosa, A. Galindo, Eur. J. Inorg. Chem. 22 (2007) 3543.
- [6] V. Suni, M.R.P. Kurup, M. Nethaji, Polyhedron 26 (2007) 3097.
- [7] B.F. Abrahams, T.A. Hudson, R. Robson, Chem. A Eur. J. 12 (2006) 7095.
- [8] C.J. Milios, A. Prescimone, J. Sanchez-Benitez, S. Parsons, M. Murrie, E.K. Brechin, Inorg. Chem. 45 (2006) 7053.
- [9] F.B. Zhang, E.M. Prokopchuk, M.E. Broczkowski, M.C. Jennings, R.J. Puddephatt, Organometallics 25 (2006) 1583.
- [10] Y.-C. Liu, C.-I. Li, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, Inorg. Chim. Acta 359 (2006) 2361.
- [11] M. Bakir, I. Hassan, O. Green, J. Coord. Chem. 59 (2006) 1953.
- [12] Y.-M. Li, S.-C. Xiang, T.-L. Sheng, J.-J. Zhang, S.-M. Hu, R.-B. Fu, X.-H. Huang, X.-T. Wu, Inorg. Chem. 45 (2006) 6577.
- [13] M.C. Suen J.C. Wang, Inorg. Chem. Commun. 9 (2006) 478.
- [14] T.C. Stamatatos, J.C. Vlahopoulou, Y. Sanakis, C.P. Raptopoulou, V. Psycharis, A.K. Boudalis, S.P. Perlepes, Inorg. Chem. Commun. 9 (2006) 814.
- [15] B. Asc, G. Alpdogan, S. Sungur, Anal. Lett. 39 (2006) 997.
- [16] Y.-C. Liu, C.-I. Li, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, Inorg. Chim. Acta 359 (2006) 2361.
- [17] X.-D. Chen, T.C.W. Mak, Inorg. Chim. Acta 359 (2006) 685.
- [18] D.R. Richardson, P.C. Sharpe, D.B. Lovejoy, D. Senaratne, D.S. Kalinowski, M. Islam, P.V. Bernhardt, J. Med. Chem. 49 (2006) 6510.
- [19] P.V. Bernhardt, P. Chin, P.C. Sharpe, D.R. Richardson, J. Chem. Soc. Dalton Trans. 30 (2007) 3232.
- [20] P.V. Bernhardt, L.M. Caldwell, T.B. Chaston, P. Chin, D.R. Richardson, J. Biol. Inorg. Chem. 8 (2003) 866.
- [21] I. Gaubeur, L.S.S. Avila-Terra, J.C. Masini, M.E.V. Suarez-Iha, Anal. Sci. 23 (2007) 1227.
- [22] M. Bakir, K. Abdur-Rashid, W.H. Mulder, Talanta 51 (2000) 735.
- [23] J.J. Pinto, C. Moreno, M. Garcia-Vargas, Talanta 64 (2004) 562.

- [24] I. Gaubeur, M.C.D. Areias, U.H.S.V. Terra, M.E.V. Suarez-Iha, Spec. Lett. 35 (2002) 455.
- [25] J.P. Juan, C. Moreno, M. Garcia-Vergas, Anal. Bioanal. Chem. 373 (2002) 844.
- [26] S. Pehkonen, Analyst 120 (1995) 2655.
- [27] S. Ianelli, M. Orcesi, C. Pelizzi, G. Pelizzi, G. Predieri, J. Organomet. Chem. 451 (1993) 59.
- [28] M. Carcelli, C. Pelizzi, G. Pelizzi, P. Mazza, F. Zani, J. Organomet. Chem. 488 (1995) 55.
- [29] C.C. Gatto, E.S. Lang, A. Kupfer, A. Hagenbach, D. Wille, U. Abram, Z. Anorg. Allg. Chem. 630 (2004) 735.
- [30] A. Bacchi, L.P. Battaglia, M. Carcelli, C. Pelizzi, G. Pelizzi, C. Solianas, M.A. Zoroddu, J. Chem. Soc. Dalton Trans. (1993) 775.
- [31] L.P. Battaglia, M.B. Ferrari, R. Boggia, Inorg. Chim. Acta 215 (1994) 85.
- [32] L. Zhao, L.K. Thompson, Z. Xu, D.O. Miller, D.R. Stirling, J. Chem. Soc. Dalton Trans. (2001) 1706.
- [33] L.P. Battaglia, P.G. Berzollo, A.B. Corradi, C. Pelizzi, J. Crystallogr. Spectrosc. Res. 23 (1993) 973.
- [34] M. Bakir, M.A.W. Lawrence, M. Singh-Wilmot, J. Coord. Chem. 60 (2007) 2385.
- [35] J. Grewea, A. Hagenbacha, B. Stromburga, R. Albertob, E. Vazquez-Lopez, U. Abrama, Z. Anorg. Allg. Chem. 629 (2003) 303.
- [36] M. Bakir, O. Brown, Inorganica Chim. Acta 353 (2003) 89.
- [37] M. Bakir, O. Brown, T. Johnson, J. Mol. Struct. 691 (2004) 265.
- [38] M. Bakir, O. Green, C. Gyles, Inorganica Chim. Acta 358 (2005) 1835.
- [39] M. Bakir, K. Abdur-Rashid, C. Gyles, Spectrochim. Acta Part A 59 (2003) 2123.
- [40] M. Bakir, K. Abdur-Rashid, Trans. Metal Chem. 24 (1999) 384.
- [41] M. Bakir, O. Brown, J. Mol. Struct. 641 (2002) 183.
- [42] M. Bakir, Eur. J. Inorg. Chem. (2002) 481.
- [43] M. Bakir, Inorg. Chim. Acta 332 (2002) 1.
- [44] M. Bakir, Acta Cryst. C57 (2001) 1371.
- [45] M. Bakir, J.A.M. McKenzie, Electroanal. Chem. 425 (1997) 61.
- [46] M. Bakir, J. Electroanal. Chem. 466 (1999) 60.
- [47] M. Bakir, O. Green, W.H. Mulder, J. Mol. Struct. 873 (2008) 17.
- [48] M. Bakir, R.R. Conry, O. Green, W.H. Mulder, J. Coord. Chem. (2008), in press.
- [49] Bruker-SMART, Software Version 5.625, Brucker AXS, Inc., Madison, Wisconsin, USA, 2001.
- [50] Bruker-SHELXTL, Software Version 5.1, Brucker AXS, Inc., Madison, Wisconsin, USA, 1997.
- [51] G.M. Sheldrick, SHELX97 and SHELXL97, University of Göttingen, Germany, 1997.
- [52] Hyper Chem 7.5 Professional Edition, Hyper Cube, Inc., 1115 NW Fourth Street, Gainesville, Florida 32601, USA.
- [53] R.M. Silverstein, F.X. Webster, Spectroscopic Identification of Organic Compounds, Sixth ed., John Wiley and Sons, Inc, 1997.