



# Coordination studies of 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine towards Zn<sup>2+</sup> cation. Synthesis and characterization by X-ray diffraction and spectroscopic methods

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We dedicate this paper to Professor Francis Sécheresse on the occasion of his 60th birthday

## Abstract

The two Zn(II) complexes Zn(dppt)Cl<sub>2</sub>·0.5 H<sub>2</sub>O (**1**) and Zn(dppt)<sub>2</sub>Cl<sub>2</sub>·2 H<sub>2</sub>O (**2**) were obtained by reaction of 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine (dppt) with zinc chloride. Complex (**2**) could be obtained from (**1**) by addition of an excess of dppt. These complexes have been characterized by 1D and 2D <sup>1</sup>H NMR spectroscopy, mass spectrometry, and in the solid state by IR and X-ray diffraction. In (**1**), the Zinc atom is bound to one ligand through the N atom of the pyridyl ring and one of the N atoms of the triazine ring, and to two chlorine atoms in a distorted tetrahedral coordination geometry. Instability of crystals of compound (**2**) (namely, the lost of crystallization solvent molecules) did not allow their analysis by X-ray diffraction. Structure and stoichiometry of (**2**) were determined by 2D COSY <sup>1</sup>H NMR and mass spectrometry. Two magnetically equivalent ligands (dppt) are coordinated to the metal center. **To cite this article:** V. Béreau *et al.*, *C.R. Chimie* 8 (2005).

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## Résumé

**Étude de la coordination du 5,6-diphényl-3-(2-pyridyl)-1,2,4-triazine avec le cation Zn<sup>2+</sup>. Synthèse et caractérisation par diffraction des rayons X et méthodes spectroscopiques.** Les deux complexes Zn(dppt)Cl<sub>2</sub>·0.5 H<sub>2</sub>O (**1**) et Zn(dppt)<sub>2</sub>Cl<sub>2</sub>·2 H<sub>2</sub>O (**2**) ont été obtenus par réaction entre le ligand 5,6-diphényl-3-(2-pyridyl)-1,2,4-triazine (dppt) et le chlorure de zinc, avec un rapport dppt/Zn(II) de 1:1 et 2:1, respectivement. Le complexe (**2**) peut également être obtenu à partir de (**1**) par addition d'un excès de ligand dppt. Des cristaux du complexe (**1**) ont été obtenus et analysés par diffraction des rayons X. Dans le complexe (**1**), l'atome de zinc est lié à un ligand dppt par l'intermédiaire de l'atome d'azote du cycle pyridyl et à un atome d'azote du cycle triazine, ainsi qu'à deux atomes de chlore, dans un environnement tétraédrique distordu. L'instabilité des cristaux du complexe (**2**), due à la perte de molécules du solvant de cristallisation, n'a pas permis leur étude par diffraction des rayons X. Sa structure a été déterminée par RMN COSY <sup>1</sup>H, en corrélation avec la spectrométrie de masse. Deux ligands (dppt)

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sont liés de manière équivalente à l'atome de Zn(II). Les deux ligands sont magnétiquement équivalents. **Pour citer cet article :** V. Béreau et al., *C.R. Chimie* 8 (2005).

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**Mots clés :** Triazine ; Complexes de zinc ; Diffraction par rayons X

## 1. Introduction

Numerous compounds containing the 1,2,4-triazine moieties are well known in natural materials and show biological, pharmacological and medicinal properties. An interesting characteristic of the derivatives of 1,2,4-triazine compounds is that they form colored complexes when they are coordinated to a metal ion. In particular, the ligand 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine, noted dppt, has been widely used as a sensitive reagent for the determination of Fe(II) by spectrophotometric methods, in natural and waste waters [1]. Its role as transfer agent for transition metal ions has been showed by electrochemistry studies [2]. Some Cu(II) complexes have been isolated and studied as potential catalytically active redox agents [3]. More recently, it has been revealed that a zinc-dppt complex associated to a biocide could have significant biocidal effects on living cells including those of microorganisms (bacteria and fungi), cell culture system, plants and animals [4]. Because of our interest in the field of the metal ion and drug interactions, we have focused our work on the synthesis and properties of Zn-dppt complexes. This paper reports the preliminary work on the preparation and the characterization by X-ray diffraction, 2D-<sup>1</sup>H NMR, infra-red and UV-vis spectroscopies of two Zn(II) complexes Zn(dppt)Cl<sub>2</sub>·0.5 H<sub>2</sub>O (**1**) and Zn(dppt)<sub>2</sub>Cl<sub>2</sub>·2 H<sub>2</sub>O (**2**).

## 2. Experimental section

Reagents and solvents were obtained commercially and used without further purification. 5,6-Diphenyl-3-(2-pyridyl)-1,2,4-triazine was commercially available from Lancaster chemicals.

### 2.1. Physical measurements

NMR spectra were obtained on a Bruker Spectrospin 200 MHz. Infrared spectra were recorded as KBr

pressed pellets on a Genesis Series FTIR Ati Mattson. UV-vis spectra were obtained from an HP8453 spectrophotometer. Measurements were made in 1 cm path length cells at 293 K. DCI and FAB mass spectra were obtained with a Nermag R10-10 spectrometer. CHN elemental analyses were performed in duplicate by Pierre Fabre Laboratories, Castres, France.

### 2.2. Synthesis of Zn(dppt)Cl<sub>2</sub>·0.5 H<sub>2</sub>O (**1**)

Dppt (209.6 mg; 0.674 mmol) and ZnCl<sub>2</sub> (93.6 mg; 0.687 mmol) were added together in a mixture of 4 ml of CH<sub>2</sub>Cl<sub>2</sub> and 2 ml of THF. The reaction solution was stirred at room temperature for 30 min. A white solid was isolated by filtration, washed with EtOH and dried with Et<sub>2</sub>O. C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>Cl<sub>2</sub>Zn·0.5 H<sub>2</sub>O, yield 180 mg, 60% based on zinc chloride. Anal. Calc. for C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>Cl<sub>2</sub>Zn·0.5H<sub>2</sub>O: C, 52.72; H, 3.10; N, 12.30. Found: C, 53.06, H, 3.34, N, 12.06%; UV-vis (EtOH) [ $\lambda_{\max}$  (nm) ( $\epsilon$  (M<sup>-1</sup> cm<sup>-1</sup>))]: 240 (14,162), 291 (19,428), 320 (sh); FT-IR (KBr) (cm<sup>-1</sup>): 538 (m), 600 (m), 696–884 (s,  $\delta_{\text{C-H}}$ ), 1013–1144 (s, Ar ring vibrations), 1375 (s), 1407 (s), 1447 (m), 1485 (m), 1518 (s), 1575 (m,  $\nu_{\text{N=N}}$ ), 1605 (s,  $\nu_{\text{C=N}}$ ), 3068 (m,  $\mu_{\text{C-H}}$ ); <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>,  $\delta$  ppm) 9.13 (br, H6), 9.09 (br, H3), 8.64 (t, H4), 8.23 (t, H5), 7.91–7.57 (m, 10H, Ar-H), mass spectrum (DCI/NH<sub>3</sub>): 409 (M-Cl), 311 (dppt). M.p. > 300 °C.

### 2.3. Synthesis of Zn(dppt)<sub>2</sub>Cl<sub>2</sub>·2 H<sub>2</sub>O (**2**)

Dppt (209.5 mg; 0.676 mmol) and ZnCl<sub>2</sub> (30.7 mg, 0.225 mmol) were stirred together at room temperature for 1 h in a mixture of 4 ml of CH<sub>2</sub>Cl<sub>2</sub> and 2 ml of THF. The yellow precipitate was filtered, washed and dried with Et<sub>2</sub>O. C<sub>40</sub>H<sub>28</sub>N<sub>8</sub>Cl<sub>2</sub>Zn·2 H<sub>2</sub>O, yield 116 mg, 70% based on zinc chloride. Anal. Calc. for C<sub>40</sub>H<sub>28</sub>N<sub>8</sub>Cl<sub>2</sub>Zn·2 H<sub>2</sub>O: C, 60.65; H, 4.04; N, 14.13. Found: C, 60.69, H, 3.73, N, 14.10%; UV-vis (EtOH)

$[\lambda_{\max} \text{ (nm)} (\epsilon \text{ (M}^{-1} \text{ cm}^{-1}))]$ : 240 (29,605), 292 (40,356), 324 (sh); FT-IR (KBr) ( $\text{cm}^{-1}$ ): 534 (m), 598 (m), 697–879 (s,  $\delta_{\text{C-H}}$ ), 1009–1113 (s, Ar ring vibrations), 1258 (w), 1372 (s), 1401 (s), 1445 (s), 1508 (s), 1600 (m,  $\nu\text{N=N}$ ), 1651 (m,  $\nu\text{C=N}$ ), 3060 (m,  $\mu\text{C-H}$ );  $^1\text{H NMR}$  (acetone- $d_6$ ,  $\delta$  ppm, ( $J$  Hz)) 9.06 (qd, 2H, H6,  $^3J_{6-5} = 4.90$ ,  $^4J_{6-4} = 1.70$ ,  $^5J_{6-3} = 1.00$ ), 8.88 (dt, 2H, H3,  $^3J_{3-4} = 7.80$ ,  $^4J_{3-5} = 1.05$ ,  $^5J_{3-6} = 1.00$ ), 8.37 (td, 2H, H4,  $^3J_{4-5} = 7.80$ ,  $^3J_{4-3} = 7.80$ ,  $^4J_{4-6} = 1.70$ ), 7.93 (qd, 2H, H5,  $^3J_{5-4} = 7.80$ ,  $^3J_{5-6} = 4.90$ ,  $^4J_{5-3} = 1.05$ ), 7.83–7.49 (m, 20H, Ar-H), mass spectrum (FAB/NBA): 721 (M-Cl), 409 (M-dppt-Cl), 311 (dppt). M.p. > 300 °C.

#### 2.4. Synthesis of $\text{Zn(dppt)}_2\text{Cl}_2 \cdot 2 \text{H}_2\text{O}$ (2) from $\text{Zn(dppt)Cl}_2 \cdot 0.5 \text{H}_2\text{O}$ (1)

Dppt (112.5 mg; 0.363 mmol) was solubilized in 2 ml of  $\text{CH}_2\text{Cl}_2$  and 1 ml of THF. To this yellow solution, (1) (54.4 mg; 0.121 mmol) was added as solid. A yellow solid started to precipitate immediately. The reaction solution was stirred at room temperature for 2 h and then filtered. The precipitate was washed with  $\text{Et}_2\text{O}$ .  $\text{C}_{40}\text{H}_{28}\text{N}_8\text{Cl}_2\text{Zn} \cdot 2 \text{H}_2\text{O}$ , yield 77 mg, 85% based on zinc chloride. Anal. Calc. for  $\text{C}_{40}\text{H}_{28}\text{N}_8\text{Cl}_2\text{Zn} \cdot 2 \text{H}_2\text{O}$ : C, 60.65; H, 4.04; N, 14.13. Found: C, 60.87, H, 3.89, N, 14.19%; UV-vis (EtOH)  $[\lambda_{\max} \text{ (nm)} (\epsilon \text{ (M}^{-1} \text{ cm}^{-1}))]$ : 239 (31,134), 290 (41,680), 320 (sh); FT-IR (KBr) ( $\text{cm}^{-1}$ ): 534 (m), 598 (m), 697–879 (s,  $\delta_{\text{C-H}}$ ), 1009–1113 (s, Ar ring vibrations), 1258 (w), 1372 (s), 1401 (s), 1445 (s), 1508 (s), 1600 (m,  $\nu\text{N=N}$ ), 1651 (m,  $\nu\text{C=N}$ ), 3060 (m,  $\mu\text{C-H}$ );  $^1\text{H NMR}$  (acetone- $d_6$ ,  $\delta$  ppm, ( $J$  Hz)) 9.05 (qd, 2H, H6,  $^3J_{6-5} = 4.90$ ,  $^4J_{6-4} = 1.70$ ,  $^5J_{6-3} = 1.00$ ), 8.86 (dt, 2H, H3,  $^3J_{3-4} = 7.80$ ,  $^4J_{3-5} = 1.05$ ,  $^5J_{3-6} = 1.00$ ), 8.33 (td, 2H, H4,  $^3J_{4-5} = 7.80$ ,  $^3J_{4-3} = 7.80$ ,  $^4J_{4-6} = 1.70$ ), 7.90 (qd, 2H, H5,  $^3J_{5-4} = 7.80$ ,  $^3J_{5-6} = 4.90$ ,  $^4J_{5-3} = 1.05$ ), 7.82–7.44 (m, 20H, Ar-H), mass spectrum (FAB/NBA): 719 (M-Cl), 409 (M-dppt-Cl), 311 (dppt). M.p. > 300 °C.

#### 2.5. X-ray structure determination

A colorless crystal,  $0.66 \times 0.20 \times 0.14 \text{ mm}^3$ , was glued to a glass fibre. Intensity data were collected at room temperature with a Siemens SMART diffractometer equipped with a CCD two-dimensional detector [ $\lambda \text{ Mo K}\alpha = 0.71073 \text{ \AA}$ ]. Slightly more than one hemisphere of data was collected in 1271 frames with  $\omega$  scans (width of  $0.30^\circ$  and exposure time of 10 s per

frame). Data reduction was performed with SAINT software. Data were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction based on symmetry equivalent reflections was applied by using the SADABS program [5]. Lattice parameters were obtained from least-squares analysis of all reflections.

The structure was solved by direct method and refined by full matrix least-squares, based on  $F^2$ , using the SHELX-TL software package [6]. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were located with geometrical restraints in the riding mode.

Crystal structure analysis: monoclinic, space group  $P2(1)/c$ ; dimensions  $a = 13.4000(2) \text{ \AA}$ ,  $b = 10.4538(1) \text{ \AA}$ ,  $c = 16.9513(2) \text{ \AA}$ ,  $\beta = 90.359(1)^\circ$ .  $V = 2374.51(5) \text{ \AA}^3$ ;  $Z = 4$ ; total reflections collected: 16,183; independent reflections: 6161 ( $3701 F_o > 4\sigma(F_o)$ ); a hemisphere of data was collected up to a  $2\theta_{\max}$  value of  $59.62^\circ$  (91% coverage). Number of variables: 283;  $R_1 = 0.0456$ ,  $wR_2 = 0.0954$ ,  $S = 1.001$ ; highest residual electron density  $0.357 \text{ e \AA}^{-3}$ .

### 3. Results and discussion

#### 3.1. Structure description

Complex (1) crystallizes in the monoclinic space group  $P2(1)/c$  with one molecule of  $\text{Zn(dppt)Cl}_2$  and one molecule of solvent (acetone) per asymmetric unit. Details of the data collection and refinement are provided in Table 1. Selected bond distances and bond angles are given in Table 2. An ORTEP [7] view of  $\text{Zn(dppt)Cl}_2 \cdot (\text{CH}_3)_2\text{CO}$  where the acetone molecule has been omitted for clarity is presented Fig. 1. In  $\text{Zn(dppt)Cl}_2 \cdot (\text{CH}_3)_2\text{CO}$ , Zn(II) is four coordinated. The Zinc atom is coordinated to the N atom of the pyridyl ring and to a N atom of the triazine ring and to two chlorine atoms. The coordination geometry is tetrahedrally distorted. The bond distances Zn–N(1) ( $2.073(2) \text{ \AA}$ ) and Zn–N(12) ( $2.069(2) \text{ \AA}$ ) are comparable with those observed in Zn-bipyridyl complexes exhibiting a distorted tetrahedral geometry, ranging from  $2.064(3)$  to  $2.113(2) \text{ \AA}$  [8]. The bond distances Zn–Cl(1) and Zn–Cl(2) are respectively,  $2.2021(9)$  and  $2.1816(9) \text{ \AA}$ . They are in accordance with those of related complexes having a  $\text{NNCl}_2$  coordination sphere

Table 1  
Crystallographic data for Zn(dppt)Cl<sub>2</sub>·(CH<sub>3</sub>)<sub>2</sub>CO

Formula	C <sub>23</sub> H <sub>20</sub> Cl <sub>2</sub> N <sub>4</sub> OZn
F <sub>w</sub>	504.70
Space group	P2(1)/c
a (Å)	13.4000(2)
b (Å)	10.4538(1)
c (Å)	16.9513(2)
α (°)	90
β (°)	90.359(1)
γ (°)	90
V (Å <sup>3</sup> )	2374.51(5)
T (°C)	273(2)
d <sub>calc</sub> (g cm <sup>-3</sup> )	1.412
Z	4
μ (Mo Kα) (cm <sup>-1</sup> )	12.81
θ range (°)	1.52–29.81
Total observations	16,183
Independent reflections	6161
R <sub>1</sub> (F)	0.0456
R <sub>w</sub> (F <sup>2</sup> )	0.0954

Table 2  
Selected bond distances (Å) and bond angles (°) for Zn(dppt)Cl<sub>2</sub>·(CH<sub>3</sub>)<sub>2</sub>CO

Zn–N(12)	2.069(2)	N(12)–Zn–N(1)	78.73(8)
Zn–N(1)	2.073(2)	Cl(1)–Zn–Cl(2)	122.80(4)
Zn–Cl(1)	2.2021(9)	N(12)–Zn–Cl(2)	111.62(7)
Zn–Cl(2)	2.1816(9)	N(1)–Zn–Cl(2)	114.81(7)
		N(12)–Zn–Cl(1)	111.87(7)
		N(1)–Zn–Cl(1)	108.60(7)
N(8)–C(9)–C(13)–C(14)	–38.3		
N(11)–C(10)–C(19)–C(24)	–36.7		
N(8)–C(7)–C(6)–C(5)	–2.7		

around the metal center (NN being a bidentate ligand) and exhibiting values in the range 2.148(4) Å–2.331(8) Å [9]. The bite angles around the metal atom range from 78.83(8) to 122.80(4)°. The distortion from ideal tetrahedral geometry and from the ideal value of 109°28' is a consequence of the opening of the two chlorine atoms due to the steric repulsion (Cl(1)–Zn–Cl(2) = 122.80(4)°) and of the small N(1)–Zn–N(12) angle (78.73(8)°). This last value is commonly observed in some Zn(II) complexes where the metal is coordinated to bidentate NN ligands in a distorted tetrahedral geometry [10,11]. The average Cl–Zn–N angle of 111.72° is also larger than the ideal value of 109°28'. The two phenyl rings at C9 and C10 of the triazine ring are not

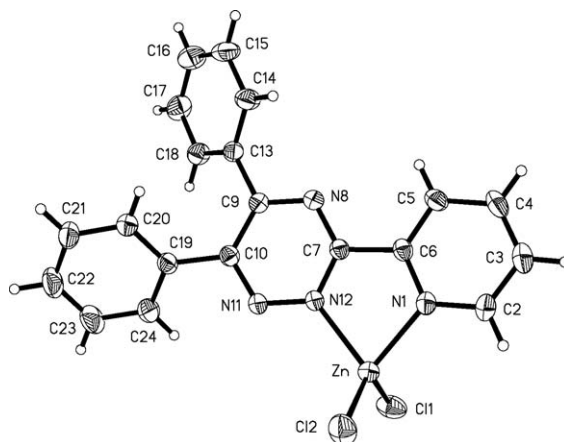


Fig. 1. ORTEP view of Zn(dppt)Cl<sub>2</sub>·(CH<sub>3</sub>)<sub>2</sub>CO. The acetone molecule has been omitted for clarity.

coplanar with the triazine plane as it is evidenced from the dihedral angles N(8)–C(9)–C(13)–C(14) and N(11)–C(10)–C(19)–C(24) which are –38.3° and –36.7° respectively. A similar distortion has been observed in 5,6-bis(4-methoxyphenyl)-3-(2'-hydroxyphenyl)-1,2,4-triazine (+41.0°) [12] and in some Ni(II) (–38.3°) [12] and Cu(II) complexes (+35.19°) of triazine derivatives [13]. In contrast, the pyridyl and the triazine rings appear almost coplanar as it is shown by the dihedral angle N(8)–C(7)–C(6)–C(5) equal to –2.7°. The coplanarity between the triazine ring and the phenyl ring in 5,6-bis(4-methoxyphenyl)-3-(2'-hydroxyphenyl)-1,2,4-triazine has also been observed with a dihedral angle of +12.1° [12]. In Zn(dppt)Cl<sub>2</sub>·(CH<sub>3</sub>)<sub>2</sub>CO, the coplanarity between the two rings to whom the coordinating N atoms belong can be explained by the coordination of the Zinc atom while in 5,6-bis(4-methoxyphenyl)-3-(2'-hydroxyphenyl)-1,2,4-triazine it was explained by an intramolecular hydrogen bond between the O atom of the phenol ring and a N atom of the triazine ring [12].

### 3.2. Synthesis and characterization

The two zinc complexes Zn(dppt)Cl<sub>2</sub>·0.5 H<sub>2</sub>O (**1**) and Zn(dppt)<sub>2</sub>Cl<sub>2</sub>·2 H<sub>2</sub>O (**2**) were prepared in a one-step reaction, mixing together 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine and zinc chloride. (**1**) and (**2**) are insoluble in the reaction media and precipitate giving yields between 60% and 70%. The isolated 85% yield of (**2**) from (**1**) as precursor is larger than that of the conventional reaction of dppt with ZnCl<sub>2</sub>. (**1**) and (**2**)

Table 3

<sup>1</sup>H NMR data for the Zn(II) complexes (1) and (2) and for the free dppt ligand. Chemical shifts values in ppm, measured in acetone-*d*<sub>6</sub>, and coupling constants values in Hz

Compound	H6	H5	H4	H3	Phenyl rings
Dppt	8.88 (d)	7.94 (t)	8.09 (t)	8.67 (d)	7.77–7.50 (m)
(1)	9.11 (br)	8.23 (t)	8.64 (t)	9.09 (br)	7.91–7.57 (m)
(2)	9.06 (qd)	7.93 (qd)	8.37 (td)	8.88 (dt)	7.83–7.49 (m)
	<sup>3</sup> J <sub>6-5</sub> = 4.90	<sup>3</sup> J <sub>5-4</sub> = 7.80	<sup>3</sup> J <sub>4-5</sub> = 7.80	<sup>3</sup> J <sub>3-4</sub> = 7.80	
	<sup>4</sup> J <sub>6-4</sub> = 1.70	<sup>3</sup> J <sub>5-6</sub> = 4.90	<sup>3</sup> J <sub>4-3</sub> = 7.80	<sup>4</sup> J <sub>3-5</sub> = 1.05	
	<sup>5</sup> J <sub>6-3</sub> = 1.00	<sup>4</sup> J <sub>5-3</sub> = 1.05	<sup>4</sup> J <sub>4-6</sub> = 1.70	<sup>5</sup> J <sub>3-6</sub> = 1.00	

are respectively a white and a yellow solid which are scarcely soluble in common organic chlorinated solvents, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and soluble in ethanol and acetone. (1) and (2) are air and moisture stable.

IR spectrum of 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine exhibits one stretching frequency for the C=N group and one stretching frequency for the N=N group: 1672 and 1614 cm<sup>-1</sup> respectively [14]. In the IR spectra of the complexes (1) and (2), these stretching vibrations appear at lower values with respect to the ν(C=N) and the of the ν(N=N) of the free ligand, 1605 and 1575 cm<sup>-1</sup> for (1) and 1651 and 1600 cm<sup>-1</sup> for (2). These observations support the coordination of one of the N atoms of the triazine ring and the N atom of the pyridyl ring to the metal ion.

The <sup>1</sup>H chemical shift are displayed in Table 3. The 2D COSY <sup>1</sup>H NMR spectrum of (2) is shown in Fig. 2. In the spectra of (1) and (2), the protons of the pyridyl rings appear as a set of four associate resonances well

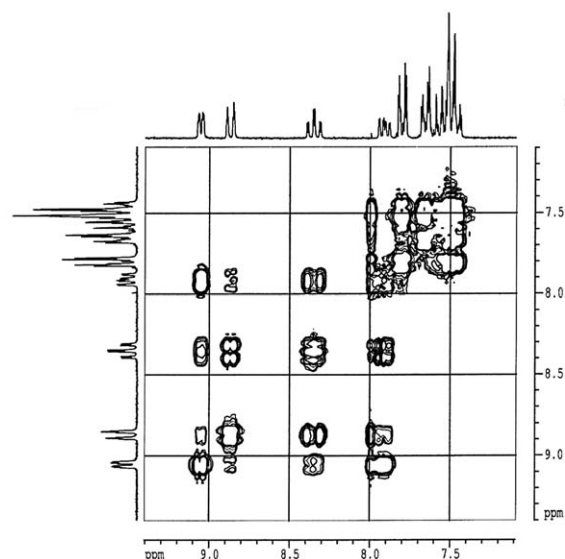


Fig. 2. 2D COSY <sup>1</sup>H NMR spectrum of (2) in acetone-*d*<sub>6</sub>.

separated from the protons of the two phenyl rings. In (1) and (2), the coordination of dppt to Zn<sup>2+</sup> produces a broadening and a displacement of the resonances down field with respect to the uncoordinated dppt ligand, as it is clearly shown in Table 3. The protons of the two phenyl rings appear in the remaining part of the spectra as two sets of multiplets, without being too much affected upon complexation. In (2), the two coordinated dppt ligands are magnetically equivalent and are symmetrically coordinated to the Zn(II) center. The <sup>1</sup>H–<sup>1</sup>H connectivities within the 2-pyridyl-1,2,4-triazine moieties were established by evaluating the COSY spectra, by measuring the different coupling constants in the 1D spectra and according literature data for the free dppt ligand [15], for Fe(II) [16], Ru(II) [17], and Re(V) [18] complexes. For illustration, complex (2) is discussed to explain the assignments. Lines are too broad in the spectrum of (1) to allow the measurement of any coupling constant. The H<sub>5</sub> proton (δ = 7.93 ppm) exhibits three correlations with H<sub>3</sub>, H<sub>4</sub> and H<sub>6</sub> that are all related by further cross peaks with H<sub>4</sub> and H<sub>6</sub>, H<sub>3</sub> and H<sub>6</sub>, and H<sub>3</sub> and H<sub>4</sub> respectively. H<sub>5</sub> is first coupled with H<sub>4</sub>: <sup>3</sup>J<sub>5-4</sub> = 7.80 Hz. The second and third coupling constants are observed with H<sub>6</sub>: <sup>3</sup>J<sub>5-6</sub> = 4.90 Hz and with H<sub>3</sub>: <sup>4</sup>J<sub>5-3</sub> = 1.05 Hz, leading to a quadruplet of doublet signal shape. H<sub>6</sub> (δ = 9.06 ppm) is coupled with H<sub>5</sub>: <sup>3</sup>J<sub>6-5</sub> = 4.90 Hz, with H<sub>4</sub>: <sup>4</sup>J<sub>6-4</sub> = 1.70 Hz and with H<sub>3</sub>: <sup>5</sup>J<sub>6-3</sub> = 1.00 Hz explaining the quadruplet of doublet shape of the H<sub>6</sub> signal. It then appears that the two coupling constants <sup>4</sup>J<sub>5-3</sub> and <sup>5</sup>J<sub>6-3</sub> (1.10 and 1.05 Hz respectively) are very closed and that the two coupling constants <sup>3</sup>J<sub>5-4</sub> = 7.80 Hz and <sup>3</sup>J<sub>3-4</sub> = 7.80 Hz are equal. That could explain the multiplicity (doublet of triplet) of the signal observed for H<sub>3</sub> (δ = 8.88 ppm), that is first correlated to H<sub>4</sub> with a coupling constant <sup>3</sup>J<sub>3-4</sub> = 7.80 Hz, and then with H<sub>5</sub> and H<sub>6</sub> with the almost same coupling constant. The remaining H<sub>4</sub> (δ = 8.37 ppm) proton is first correlated via a triplet to H<sub>5</sub>



and H<sub>3</sub> with  ${}^3J_{4-5} = 7.80$  Hz and  ${}^3J_{4-3} = 7.80$  Hz. The triplet is then split in a triplet of doublet due to the connectivity with H<sub>6</sub>:  ${}^4J_{3-6} = 1.70$  Hz.

Chemical ionization mass spectrum of (1) exhibits two fragments, one corresponding to the loss of one chloride ion:  $[\text{Zn}(\text{dppt})\text{Cl}]^+$  at  $m/z = 409$ , and the other one being the fragment of the free dppt at  $m/z = 311$ . For (2), the FAB mass spectrum is mainly characterized by three fragments. The first one, at  $m/z = 721$ , characterizes the loss of one chloride ion leading to the fragment  $[\text{Zn}(\text{dppt})_2\text{Cl}]^+$ . The loss of one dppt ligand associated with the loss of one chloride ion is also observed with fragments  $[\text{Zn}(\text{dppt})\text{Cl}]^+$  appearing at  $m/z = 409$ . The last fragment obtained is the free dppt ligand at  $m/z = 311$ . These results are in agreement with the two proposed chemical formula for (1) and (2).

In summary, we have synthesized and fully characterized two Zn(II) complexes of the 5,6-diphenyl-3-(2-pyridyl)-1,2,4-triazine. The different spectral characterizations coupled with the X-ray diffraction for (1) have shown the coordination of one ligand in (1) and the symmetrically coordination of two ligands in (2) through the N atom of the pyridyl ring and one of the N atom of the triazine ring. The lability of the two chlorine atoms and the possibility of coordinating a second ligand to the Zinc atom in  $\text{Zn}(\text{dppt})\text{Cl}_2$  (1) will lead us to study the combination effects potentially produced by a mixture of the isolated  $\text{Zn}(\text{dppt})\text{Cl}_2$  complex reported herein and different drugs on the killing or inhibiting the growth of living cells.

#### 4. Supplementary material

The CIF format file for  $\text{Zn}(\text{dppt})\text{Cl}_2 \cdot (\text{CH}_3)_2\text{CO}$  has been sent to Cambridge Crystallographic Data Center, 12 Union road, Cambridge CB21EZ, UK as supplementary materials No. SUP 238194 and can be obtained

by contacting the CCDC (quoting the article details and the corresponding SUP number).

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