Synthesis and physico-chemical studies of a novel coordination compound $ZnCl_2(C_6H_4FNH_2)_2$

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ABSTRACT

A new Zn(II) complex with the monodentate ligand 3-fluoroaniline, $ZnCl_2(C_6H_4FNH_2)_2$, has been prepared and characterized by single crystal X-ray diffraction, Solid state NMR, IR and UV-visible spectroscopies. The Zn(II) ion, located on a special position, is tetracoordinated by two nitrogen atoms of two 3-fluoroaniline monodentate ligands and two chlorine ligands. In the atomic arrangement, the $ZnCl_2(NH_2)_2$ entities are interconnected via N-H…Cl hydrogen bonds to form inorganic layers parallel to the (b, c) plane. The organic 3-fluorophenyl groups are located between these layers and connect each other via C-H…F hydrogen bonds to perform an infinite three-dimensional network. The F atom of the 3-fluoroaniline ligand is disordered over two positions. An F-F interaction between neighboring fluorine atoms contributes also to the structure cohesion. The ^{13}C and ^{15}N CP-MAS NMR spectra are in agreement with the X-ray structure. DFT calculations allow the attribution of the carbon peaks to the different independent atoms. Solid-state UV-Vis spectrum of the complex has been assigned to ligand and charge transfer transitions.

Indexing terms/Keywords

X-ray diffraction; Crystal structure; IR spectroscopy; CP-MAS NMR; DFT calculations.

INTRODUCTION

In recent years, a great effort has been devoted to the self-assembly of organic and inorganic molecules in the solid state. In this domain, the synthesis and characterization of metal organic frameworks has been an active area of research in coordination chemistry [1]. This arises not only from the fundamental properties of these materials such as their intriguing topological frameworks, but also from their unexpected potential applications in a wide range of various fields such as engineering, device manufacturing, materials science, … [2-5]. In this area, transition metal complexes are known to be effective against rheumatoid arthritis and they also show anti-ulcer activity [6, 7]. These complexes have different molecular geometries, such as tetrahedral, square planar, square pyramidal, trigonal bipyramidal and octahedral [8].

As a contribution to the investgation of the above materials, we report here the crystal structure and the physico-chemical characterization of one such compound, $ZnCl_2(C_6H_4FNH_2)_2$, formed from the reaction of the 3-fluoroaniline and the zinc chloride.

2. Experiment

2.1. Chemical preparation

A solution of $ZnCl_2$ (27.2 mg, 0.2 mmol) in water was added dropwise to a solution of 3-fluoroaniline (24.2 mg, 0.2 mmol) in ethanol (6 mL). After stirring during 30 min, the mixture was filtered. Crystals suitable for X-ray analysis were obtained after five days by slow evaporation of the filtrate at room temperature (yield = 65 %).

2.2. Investigation techniques

The characterization of the title compound was carried out by X-ray diffraction, solid state NMR, DFT calculations, IR and UV-visible spectroscopies.

2.2.1. X-ray single crystal structural analysis

A single crystal was carefully selected in order to perform its structural analysis by X-ray diffraction. The intensity data were collected on a Super Nova diffractometer using ω scan technique with CuKα radiation (λ = 1.54184 Å). The structure was solved with direct methods using the SIR97 program [9] and refined with full-matrix least-squares techniques using SHELX97 [10]. The drawings were made with Diamond [11]. Crystal data and experimental parameters used for the intensity data collection are summarized in Table 1.

2.2.2. Physical measurements

The NMR spectra were recorded on a solid-state high-resolution Bruker DSX-300 spectrometer operating at 75.49 MHz for ^{13}C and 30.30 MHz for ^{15}N with a classical 4 mm probehead allowing spinning rates up to 10 kHz. ^{13}C and ^{15}N NMR chemical shifts are given relative to tetramethylsilane and liquid ammonia, respectively (precision 0.5 ppm). The spectra were recorded by use of cross-polarization (CP) from protons (contact time 5 ms) and MAS. Before recording the spectrum it was checked that there was a sufficient delay between the scans allowing a full relaxation of the protons. The IR spectrum was recorded in the range 4000 - 400 cm^{-1} with a "Perkin-Elmer FTIR" spectrophotometer 1000 using a sample dispersed in spectroscopically pure KBr pressed into a pellet. The UV-visible spectrum was recorded on a UV-3101PC scanning spectrophotometer.

Table 1. Experimental details

Crystal data	
$C_{12}H_{12}Cl_2F_2N_2Zn$	F(000) = 720
M_r = 358.53	D_x = 1.738 Mg m^{-3}
Monoclinic, C2/c	CuKα radiation, λ = 1.5418 Å
Hall symbol: -C 2yc	Cell parameters from 8704 reflections
a = 26.4062 (6) Å	θ = 3.5 - 76.2°
b = 4.7009 (1) Å	μ = 6.18 mm^{-1}
c = 11.4741 (2) Å	T = 110 K
β = 105.819 (2)°	Prismatic, colorless
V = 1370.37 (5) Å^3	0.27 × 0.14 × 0.07 mm
Z = 4	

Data collection

SuperNova, Dual, Cu at zero, Atlas diffractometer	1434 independent reflections
Radiation source: SuperNova (Cu) X-ray Source	1423 reflections with I > 2σ(I)
Mirror monochromator	R_{int} = 0.020
Detector resolution: 10.4508 pixels mm^{-1}	θ_{max} = 76.4°, θ_{min} = 3.5°
ω scans	h = −32→32
Absorption correction: analytical	k = −5→5
T_{min} = 0.354, T_{max} = 0.709	l = −14→14
12830 measuredreflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)]$ = 0.018	Hydrogen site location: difference Fourier map
$wR(F^2)$ = 0.049	H atoms treated by a mixture of independent and constrained refinement
S = 1.05	w = $1/[\sigma^2(F_o^2) + (0.0276P)^2 + 1.5545P]$ where P = $(F_o^2 + 2F_c^2)/3$
1434 reflections	$(\Delta/\sigma)_{max}$ < 0.001
105 parameters	$\Delta\rho_{max}$ = 0.28 e Å^{-3}
0 restraints	$\Delta\rho_{min}$ = −0.26 e Å^{-3}

3. Results and discussion

3.1. Structure description

The main geometrical features of the different chemical entities of the coordination compound $ZnCl_2(C_6H_4FNH_2)_2$ are reported in Tables 2 and 3.

The asymmetric unit of the title compound, $ZnCl_2(C_6H_4FNH_2)_2$, consists of one half of Zn(II) cation, one chlorine anion and one 3-fluoroaniline molecule (Fig. 1). The Zn(II) ion, which is located on a special position, is tetracoordinated by two nitrogen atoms of two 3-fluoroaniline monodentate ligands and two chlorine ligands. The detailed geometry of the $ZnCl_2N_2$ unit (Table 2) shows that the bond angles around the Zn atom vary between 108.07(3) and 113.87(6)°, indicating that the $ZnCl_2N_2$ species has a slightly distorted tetrahedral stereochemistry (Fig. 2). The tetrahedron is less distorted than in 4-(3,5-diphenyl-1*H*-pyrazol-1-yl)-6-(piperidin-1-yl) pyrimidine dichlorozincate, where the bond angles around the Zn atom in $ZnCl_2N_2$ moiety range from 79.5(1) to 116.1(1)° [12].

In the atomic arrangement, the $ZnCl_2(NH_2)_2$ entities are interconnected via N-H…Cl hydrogen bonds to form inorganic layers parallel to the (b, c) plane (Fig. 3). Two such layers cross the unit cell at x = n/2 and the bodies of the organic entities are located between these layers and connect each other via C-H…F hydrogen bonds to perform an infinite three-dimensional network (Fig. 4, Table 3).

Examination of the organic entity geometrical features (Table 2) shows that the 3-fluoroaniline molecule exhibits a regular spatial configuration with C-C and C-N distances and C-C-C and C-C-N angles quite similar to those found in aniline derivatives [13]. The organic entity is characterized by a statistical disorder, showing two partial atoms in unequal proportions (0.408 (3) : 0.592 (3)), F8 and F9, respectively. This statistical fluorine disorder was already observed in the organo-metallic compound $[Ni(C_{13}H_9FNO)_2(C_5H_5N)_2]$, where the fluorine proportions are 0.700 (4) and 0.300 (4) [14]. It is worth noticing that no π-π stacking interactions between neighboring aromatic rings or C-H…π interactions towards them are observed.

In the structure of the title compound, the shortest distance between the fluorine atoms is 2.888 (1) Å (Fig. 5), which is smaller than the sum of the Van der Waals radii, equal to 2.94 Å, indicating the presence of fluor-fluor interaction [15].

Table 2. Selected geometric parameters (Å, º)

Zn1 - N7	2.047 (1)	Zn1 - Cl1^i	2.2514 (3)
Zn1 - N7^i	2.047 (1)	Zn1 - Cl1	2.2514 (3)
N7 - Zn1 - N7^i	113.87 (6)	N7 - Zn1 - Cl1	108.07 (3)
N7 - Zn1 - Cl1^i	109.07 (3)	N7^i - Zn1 - Cl1	109.07 (3)
N7^i- Zn1 - Cl1^i	108.07 (3)	Cl1^i - Zn1 - Cl1	108.58 (2)
C3 - C4	1.381 (2)	C5 - C4	1.381 (2)
C3 - C2	1.384 (2)	C2 - C1	1.388 (2)
C6 - C5	1.3840 (2)	N7 - C1	1.444 (2)
C6 - C1	1.388 (2)		
C3 - C4 - C5	117.6 (1)	C4 - C3 - C2	122.2 (1)
C3 - C2 - C1	118.5 (1)	C5 - C6 - C1	118.2 (1)
C4 - C3 - C2	122.2 (1)	C4 - C3 - C2	122.2 (1)

Symmetry code : (i) −x, y, −z+1/2.

Table 3. Selected hydrogen-bond interactions.

D-H…A	D-H(Å)	H…A(Å)	D…A(Å)	D-H…A (°)
N7 - H7A…Cl1^{II}	0.89 (2)	2.50 (2)	3.368 (1)	164 (2)
N7H-7B…Cl1^{III}	0.88 (2)	2.56 (2)	3.371 (1)	153 (2)
C2 - H2…F9^{IV}	0.95	2.62	3.446 (2)	146
C3 - H3…F8^V	0.95	2.68	3.413 (3)	135
C4 - H4…F8^{VI}	0.95	2.67	3.214 (3)	117

Symmetry codes : (ii) x, −y+1, z−1/2; (iii) x, y+1, z; (iv) x, −y+1, z+1/2; (v) −x+1/2, −y+3/2, −z+1; (vi) −x+1/2, −y+1/2, −z+1.
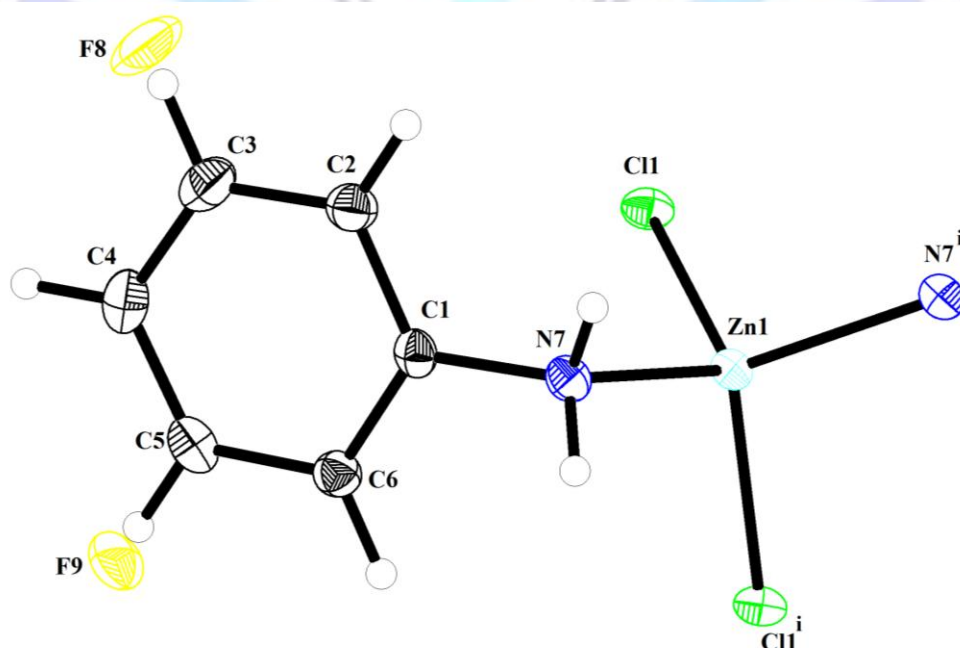

Figure. 1 Asymmetric unit of ZnCl$_2$(C$_6$H$_4$FNH$_2$)$_2$ with the atom numbering scheme and thermal ellipsoids at 50 % probability. Symmetry code :(i) 1-x, y, 0.5-z. Hydrogen bonds are shown as dashed lines.
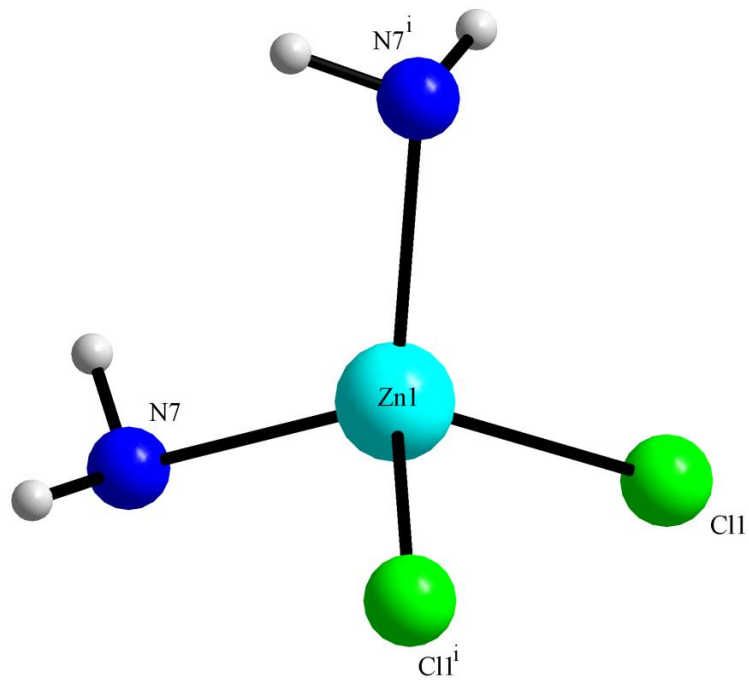
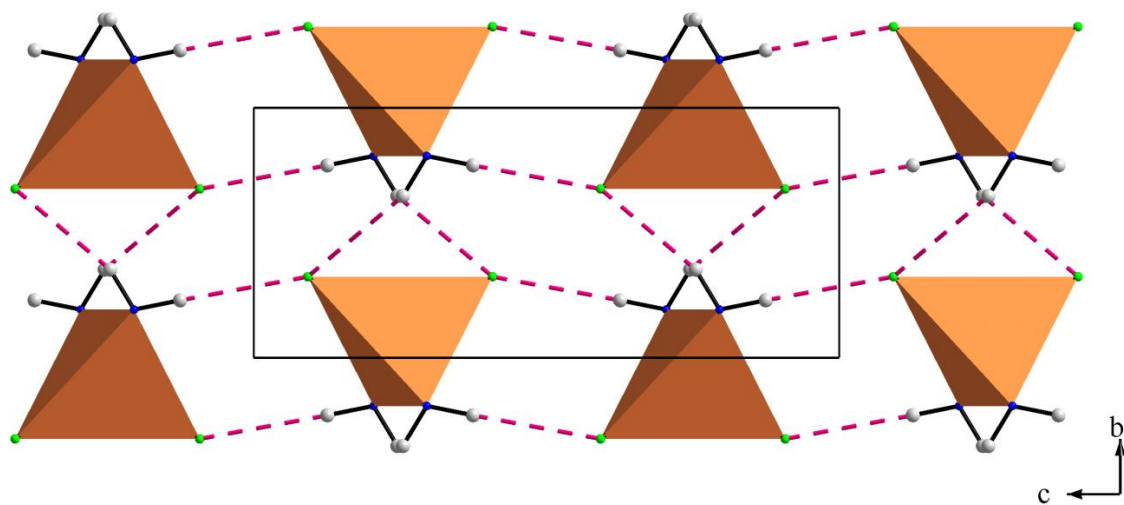**Figure. 2 Geometry around the Cu(II) cation in ZnCl$_2$(C$_6$H$_4$FNH$_2$)$_2$. Symmetry code : (i) 1-x, y, 0.5-z.**

Figure. 3 Inorganic layer in ZnCl$_2$(C$_6$H$_4$FNH$_2$)$_2$. Organic radicals are omitted for figure clarity. The dotted lines indicate hydrogen bonds.
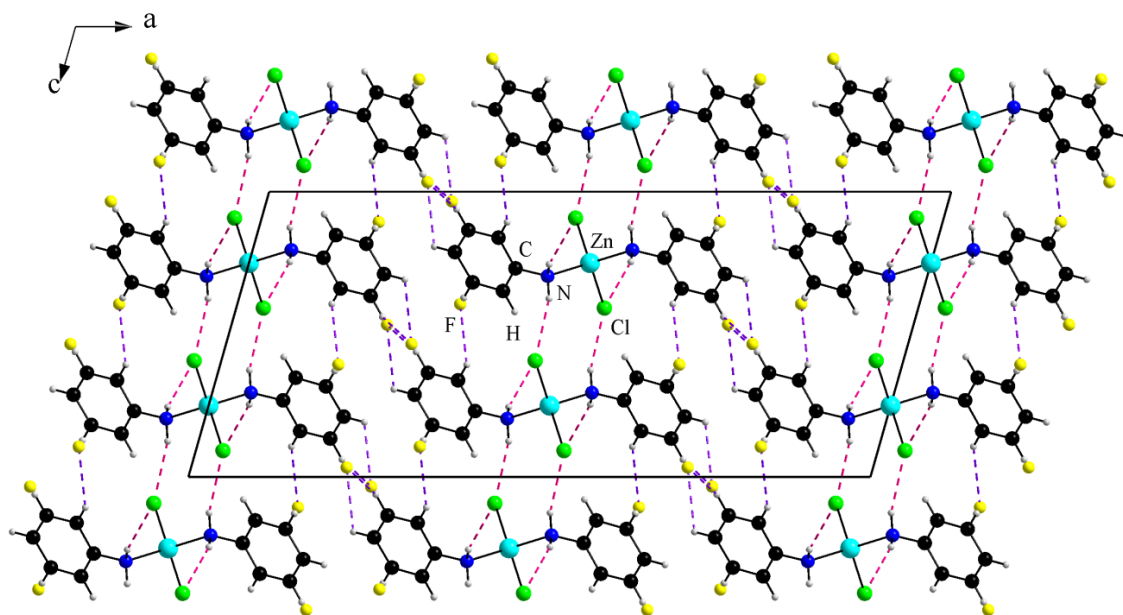
Figure. 4 A projection of the structure of ZnCl$_2$(C$_6$H$_4$FNH$_2$)$_2$ along the *b*-axis. The dotted lines indicate hydrogen bonds.

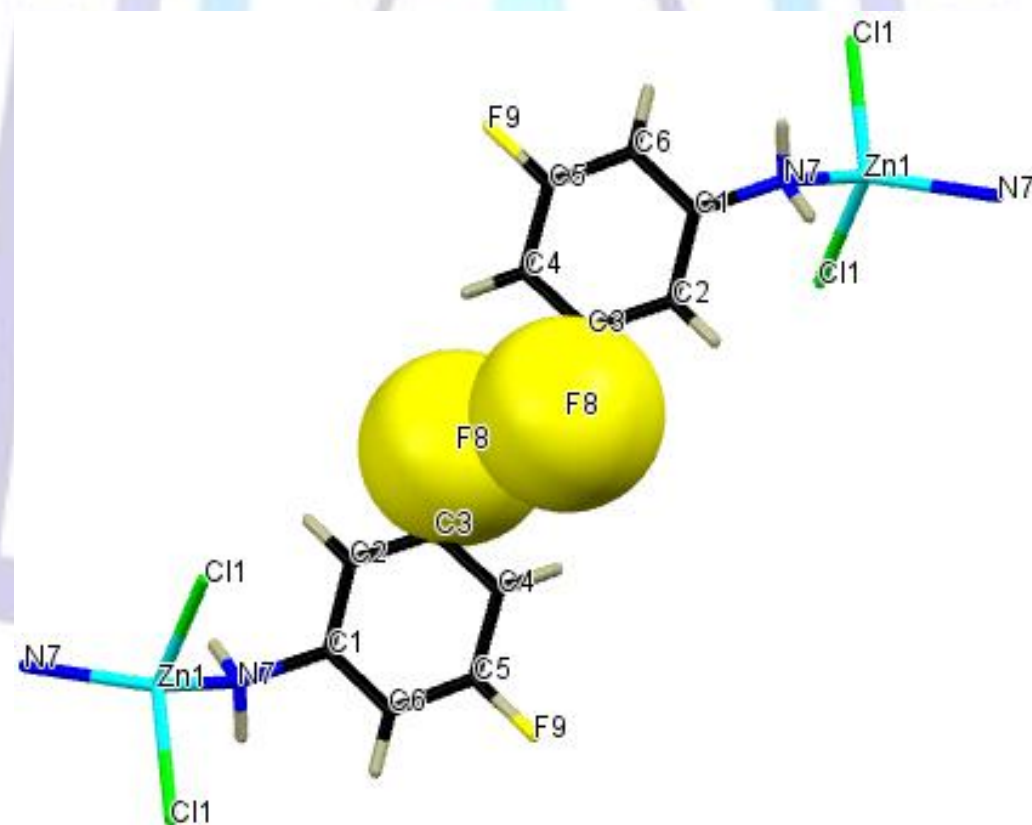**Figure. 5 F – F interaction in ZnCl$_2$(C$_6$H$_4$FNH$_2$)$_2$.**

3.2 NMR spectroscopy

The ^{13}C CP-MAS NMR spectrum of the title compound is shown on Figure 6. It displays seven well-defined resonances, in agreement with only one organic molecule in the asymmetric unit cell. Theoretical calculations were undertaken in order to assign the NMR resonances to the different crystallographically unequivalent carbon atoms of the unit cell. These calculations were made at the B3LYP/6-31+G* level. Three different calculations were made on the organic cation and in all cases the theoretical chemical shifts were subtracted from those of the reference (tetramethylsilane) calculated at the same level of theory:

(1) Calculation of the NMR chemical shifts (with the GIAO method) by using the positions of atoms obtained by X-ray diffraction;

(2) Optimization of the positions of the protons in the above molecule and calculation of the NMR chemical shifts in this semi-optimized geometry. Indeed X-ray diffraction leads always to underestimated X-H bond lengths, due to the fact that it is sensitive to the electronic cloud and does not see the nuclei;

(3) Full optimization of all atoms and calculation of NMR chemical shifts. This calculation, compared to the above one will give indications on the steric hindrance around the organic cation and on the positions where it is the strongest.
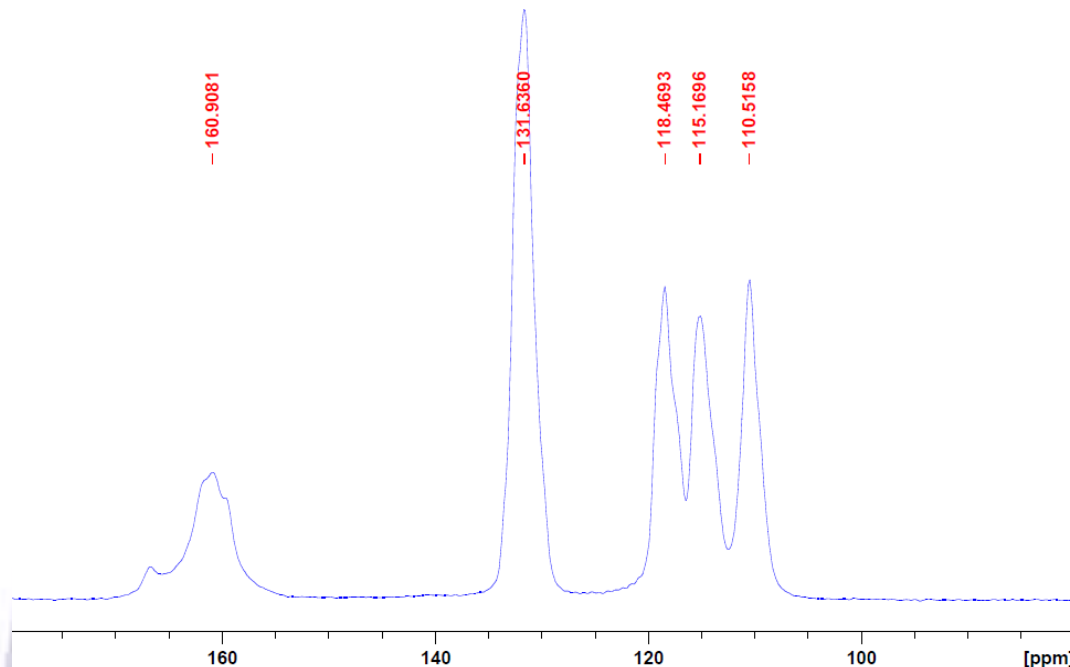

Figure. 6 ^{13}C CP-MAS NMR spectrum of ZnCl$_2$(C$_6$H$_4$FNH$_2$)$_2$.

The results are listed in Table 4, while Figure 7 shows the correlation between experimental and calculated values (after optimization of the protons positions). Clearly, there is a good agreement between the experimental and theoretical values calculated after optimization of the position of the protons, allowing unambiguously the attribution of the different NMR signals. It should be noted that the high-field gap is due to the fact that the proposed C3 carbon signal is one of the two components of the doublet due to the coupling carbon-fluorine (a typical value of this coupling is 240 Hz corresponding to 3.25 ppm for the spectrometer used for these studies).
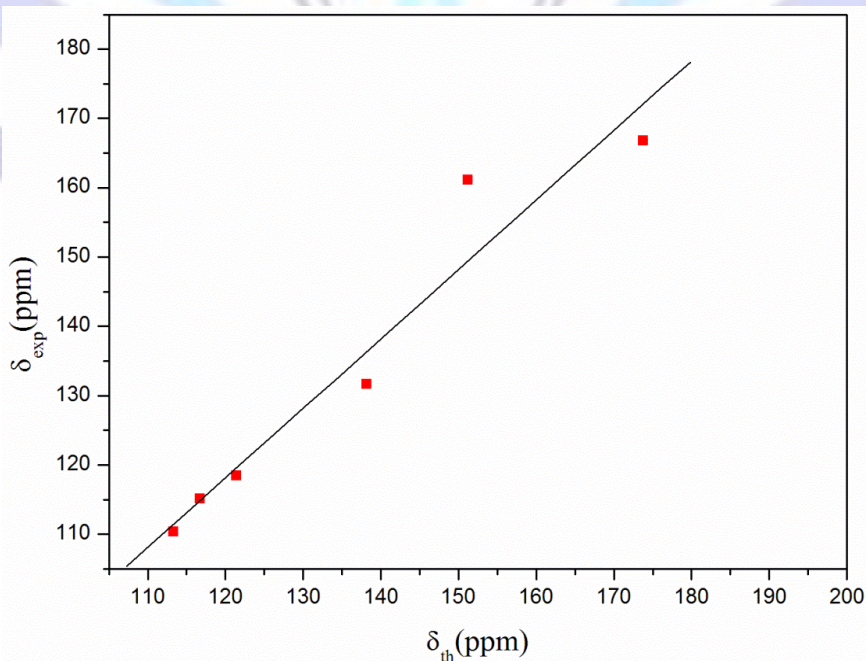

Figure. 7 Comparison between experimental and calculated carbon-13 chemical shifts in ZnCl$_2$(C$_6$H$_4$FNH$_2$)$_2$.

Table 4. Chemical shift values of the carbon atoms in $ZnCl_2(C_6H_4FNH_2)_2$. P = 0.592 corresponds to the organic molecule containing the fluorine atom attached to the C5 carbon atom and P = 0.408 is related to the moiety where the fluorine atom is bonded to the C3 atom.

Atom	X-rays		optimisation of protons		full optimisation	Experimental
	P = 0.592	P = 0.408	P = 0.592	P = 0.408		
C1	148.6	149.7	148.8	149.8	151.2	161.1
C2	107.0	108.5	111.8	113.7	113.3	110.4
C3	173.9	171.3	172.1	169.6	173.8	166.8
C4	111.3	109.9	116.0	114.6	116.7	115.2
C5	130.9	132.1	135	136.1	138.2	131.7
C6	116.4	114.3	122	119.5	121.4	118.5

The ^{15}N CP-MAS NMR spectrum of the title compound (Fig.8) is also in good agreement with the X-ray structure. Indeed, it exhibits a single resonance at 41.4 ppm corresponding to only one crystallographic site.
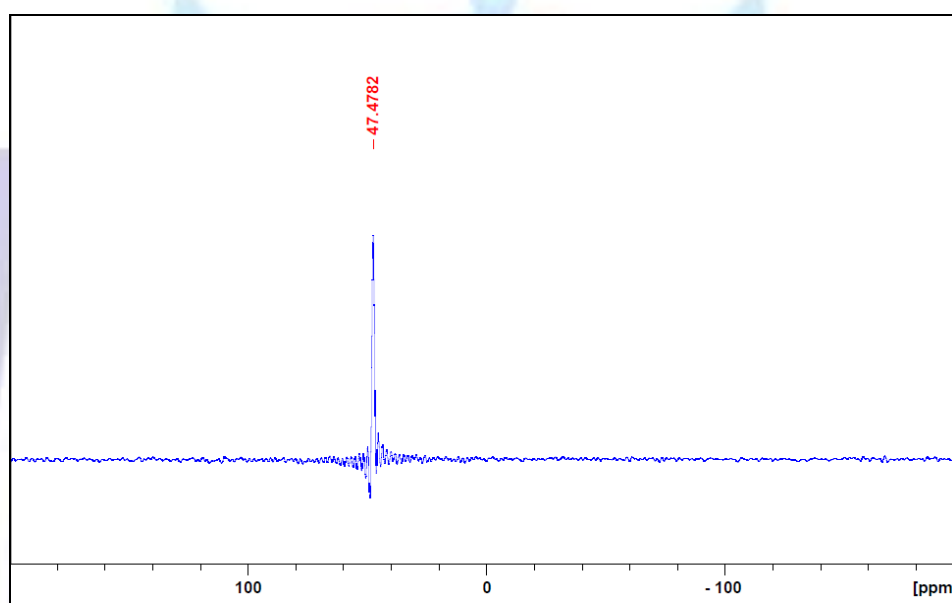

Figure. 8 ^{15}N CP-MAS NMR spectrum of $ZnCl_2(C_6H_4FNH_2)_2$.

3.3 IR absorption spectroscopy

The IR spectrum of crystalline $ZnCl_2(C_6H_4FNH_2)_2$ is shown in Figure 9. The most representative and characteristic vibrational modes of this compound can be compared to those of similar complexes [16-18]. Some aspects of the performed assignments are briefly commented as follows:

- In the high-frequency region, the broad bands between 3600 and 2500 cm^{-1} corresponds to the valence vibrations of C-H and N-H groups [19].

- The observed bands in the 1630-1100 cm^{-1} region can be attributed to the bending vibrations of N-H groups and to the valence vibrations of C=C of the aromatic ring and to stretching and bonding modes of the 3-fluoroaniline ligand ν(C-C), ν(C-N), ν(C-H)and ν(N-N) groups [20, 21].

- The band related to the stretching mode of the C-F group is observed at 1135 cm^{-1} [22].

- The bands between 1000 and 600 cm^{-1} are assigned to the out of plane bending modes γ(C_{ary}-H), γ(C_{ary}-C) and γ(N-H) [23].
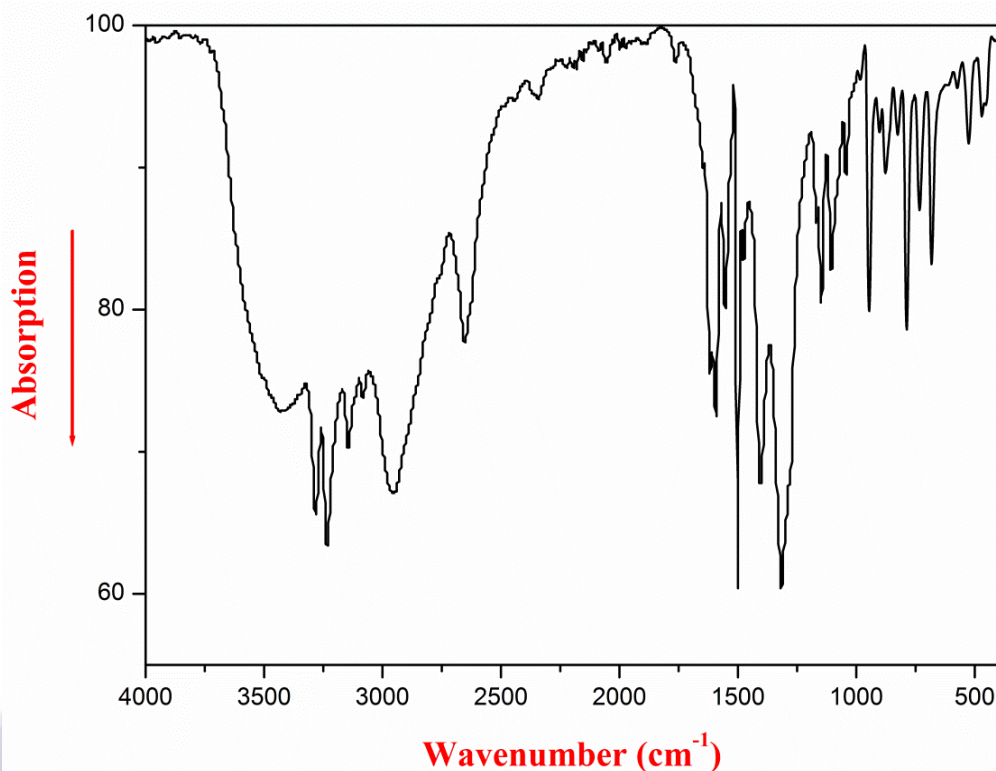
Figure. 9 IR absorption spectrum of the title compound.

3.4 UV-vis Spectroscopy

The solid state UV-vis spectrum of crystalline $ZnCl_2(C_6H_4FNH_2)_2$is shown in Figure 10. The absorbing bond at 298 nm is assigned to the n→π* electron transition of the coordinated ligand [24, 25], while the corresponding band of the free ligand occurs at 295 nm. As the ligand has no band at wavelengths higher than 300 nm and the metal has no d-d transition, the band at 350 nm must be attributed to a charge transfer of metal to ligand (MLCT), showing the formation of a Zn-N bond [26].
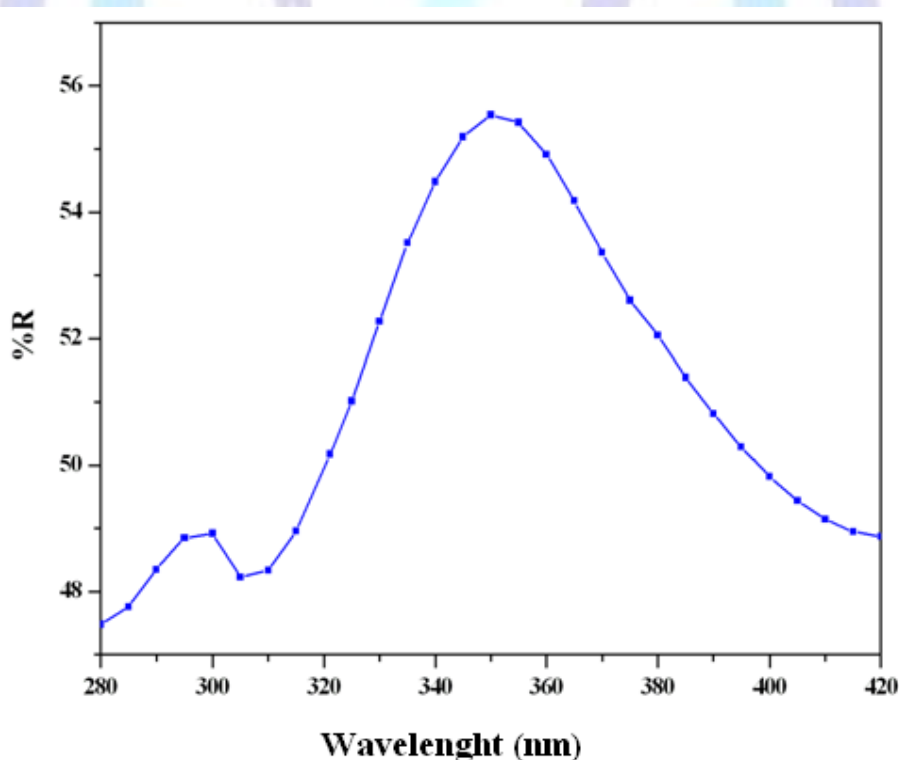

Figure. 10 Solid state UV-visible spectrum of $ZnCl_2(C_6H_4FNH_2)_2$. R = total reflectivity.

4. Conclusions

A new Zn(II) complex with the monodentate ligand 3-fluoroaniline, $ZnCl_2(C_6H_4FNH_2)_2$, was synthesized and characterized by various physico-chemical methods. At the structural level, the atomic arrangement of this material consists of inorganic layers built by the $ZnCl_2(NH_2)_2$ units interconnected via N-H…Cl hydrogen bonds. The bodies of the organic entities are located between these layers and connect each other via C-H…F hydrogen bond. In this complex the Zn atom has a slightly distorted tetrahedral environment. The F atom of the 3-fluoroaniline ligand is disordered over two positions. An F-F interaction between neighboring fluorine atoms has been observed. The number of ^{13}C and ^{15}N CP-MAS NMR lines is in full agreement with crystallographic data. The solid-state UV-Vis spectrum of the complex has been assigned to ligand and charge transfer transitions.

Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No 1013990. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

Acknowledgments

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