Synthesis, structure and characterization of a new noncentrosymmetric Zn(II) complex with the 2-amino-5-chloropyridine ligand (ACIPy)

Wijdene Nbili[a], Kamel Kaabi[a], Valeria Ferretti[b], Frédéric Lefebvre[c], Chérif Ben Nasr[a]*

[a] Laboratoire de Chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisie,

[b] Department of Chemical and Pharmaceutical Sciences and Center for Structural Diffractometry, via Fossato di Mortara 17, I-44121 Ferrara, Italy

[c] Laboratoire de Chimie Organométallique de Surface (LCOMS), Ecole Supérieure de Chimie Physique Electronique, 69622 Villeurbanne Cedex, France.

Correspondence email: cherif_bennasr@yahoo.fr

ABSTRACT

A new noncentrosymmetric Zn(II) complex with the monodentate ligand 2-amino-5-chloropyridine (ACIPy), $ZnCl_2(C_5H_5ClN_2)_2$, has been prepared at room temperature and characterized by single crystal X-ray diffraction, ^{13}C CP-MAS-NMR and IR spectroscopies. The basic coordination pattern of the ACIPy coordinated metal cations is slighly distorted tetrahedral. The crystal structure is characterized by $ZnCl_2N_2$ tetrahedra interconnected via N-H⋯Cl hydrogen bonds generated by the NH_2 amino group to form chains extending along the (a-c) direction. The exocyclic N atom is an electron receiving center, which is consistent with features of imino resonance as evidenced by bond lengths and angles. The crystal structure is stabilized by sets of intra and intermolecular hydrogen bonds. The ^{13}C CP-MAS NMR spectrum is discussed and the vibrational absorption bands are identified by infrared spectroscopy and theoretical calculations.

Indexing terms/Keywords

X-ray diffraction; Crystal structure; ^{13}C CP-MAS NMR IR spectroscopy; IR spectroscopy; DFT calculations.

Council for Innovative Research

INTRODUCTION

The design and fine tuning of ligands are extremely important aspects of coordination chemistry. Among ligands commonly used in coordination chemistry, Schiff bases are an extremely important class, thanks to their facile synthesis, and easily tunable steric and electronic properties [1, 2]. They are known to be a class of versatile ligands, allowing to generate a variety of molecular architectures and coordination polyhedra [3-5]. The metal complexes of such Schiff bases have been extensively used as biological probes [6], DNA cleaving agents [7], catalysts [8, 9], sensing materials [10, 11] and corrosion inhibitors [12]. In recent years, the coordination chemistry of N coordinated ligands has also received a lot of attention because of their relevance to biological systems [13].

Recently, a molecular engineering strategy has been developed that aims at building very coive acentric crystalline structures for nonlinear optics based on the encapsulation of organic chromophores in inorganic host matrices [14]. The design of organic aromatic conjugated compounds and organic-inorganic polar crystals has been studied for over twenty years because some of them exhibit nonlinear optical coefficients [14-16]. In this type of materials, the nonlinear optical response can be explained primarily by an anharmonic distortion of the electron density distribution inside the molecules due to the intense electric field of the applied optical pulse [17].

As part of our continued involvement in the investigation of metal complexes of nitrogen containing ligands such as Schiff bases [18], we report here the synthesis and the characterization of a new Zn(II) complex with the monodentate ligand 2-amino-5-chloropyridine)], ACIPy. This compound, which crystallizes in a non-centrosymmetric space group, could be a good candidate material for nonlinear optical applications.

2. Experiment

2.1. Chemical preparation

A solution of $ZnCl_2$ (28 mg, 0.2 mmol) in water (10 mL) was added dropwise to a solution of 2-amino-5-chloropyridine (52 mg, 0.4 mmol) in ethanol (10 mL). After stirring for 45 min, the mixture was filtered and the resultant solution allowed to evaporate at room temperature. Crystals of the title compound, which remained stable under normal conditions of temperature and humidity, were isolated after several days and subjected to X-ray diffraction analysis (yield 67%).

2.2. Investigation techniques

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

2.2.1. X-ray diffraction

A single crystal was carefully selected under polarizing microscope in order to perform its structural analysis by X-ray diffraction. The crystallographic data were collected on a Nonius Kappa CCD diffractometer at room temperature using graphite-monochromated MoKα radiation (λ= 0.71073 Å). Data set was corrected for Lorentz-polarization and absorption effects [19]. The crystal parameters and other experimental details of the data collection are summarized in Table 1. The structure was solved by direct methods (SIR97) [20] and refined by full-matrix least-squares methods with all non-hydrogen atoms anisotropic. Hydrogens were included on calculated positions, riding on their carrier atoms, apart from those belonging to the amino groups, that were localized in the difference Fourier map and optimized to restrained positions. The Flack parameter [21] is -0.020(10), indicating that the atomic arrangement corresponds to the absolute structure.

All calculations were performed using SHELXL-97 [22] implemented in the WINGX system of programs [23]. Selected bond distances and angles and geometrical parameters for hydrogen bonding interactions are given in Tables 2 and 3, respectively. We have considered only contacts where C-H…X angles are greater than 130° and H…X distances are shorter than the sum of the van der Waals radii. The drawings were made with Diamond [24] and OrtepIII [25].

2.2.2. Infrared spectroscopy

IR spectra were recorded in the range 4000 - 400 cm^{-1} with a ''Perkin-Elmer FT-IR-1000'' spectrophotometer using samples dispersed in spectroscopically pure KBr pellets.

2.2.3. DFT calculations

The calculations were made with the Gaussian A.09 software by use of the B3LYP method. The basis set was 6-31+G* for all atoms. The calculations were made on the Zn complex with two chlorine and two organic ligands. Three types of calculations were made (see below) and in each case both the NMR chemical shifts and the IR spectrum were calculated.

Table 1.Experimental details

Crystal data	
Chemical formula	$C_{10}H_{10}Cl_4N_4Zn$
M_r	393.39
Crystal system, space group	Monoclinic, Cc
a, b, c (Å)	12.8854 (4), 15.2961 (5), 7.8566 (3)
β (°)	103.047 (1)
V (Å^3)	1508.53 (9)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	2.33
Crystal size (mm)	0.26 × 0.20 × 0.11
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	11668, 3678, 2571
R_{int}	0.064
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.032, 0.061, 0.96
No. of reflections	3678
No. of parameters	189
No. of restraints	6
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.54, −0.70

3. Results and discussion

3.1. Structure description

Figure 1 reports the ORTEPIII diagram for the title compound, while relevant geometrical parameters are reported in Table 2. The asymmetric unit consists of a Zn(II) complex where the cation is coordinated to two chlorine anions and two monodentate 2-amino-5-chloropyridine (AClPy) neutral ligands (Fig. 1); the coordination geometry can be described as slightly distorted tetrahedral. A quantification of the distortion is provided by the values of the 'quadratic elongation' λ and 'angle variance' σ^2 parameters, which, according to Robinson et al. [26], assume a value of 1 and 0, respectively, in a perfect tetrahedron: in the present structure, for a polyhedral volume of 4.95 Å^3, λ and σ^2 have been calculated to be 1.01 and 32.60, respectively. These parameters are strictly comparable with those calculated for the three Zn-dichloro similar complexes retrieved from CSD [27, 28] which show an identical λ value of 1.01 and σ^2 values ranging from 8.34 to 29.17. Zn-N and Zn-Cl bond distances (Table 2) are similar to those reported for other tetrahedral Zn(II) complexes with similar Schiff bases [29]. The bond valence calculations gives a value of 1.92 for the Zn cation [30] in agreement with the +2 oxidation state.

The sum of the angles around the N(3) and N(4) nitrogen atoms are close to 360° and the C-N distances of the NH$_2$ groups are 1.344(4) Å for the N(3)-C(1) and 1.369(5) Å for N(4)-C(6), which are short for C-N single bonds, but still not quite as contracted as one would expect for a full established C=N double bond. These bond length features are consistent with an imino resonance form as it is commonly found for a C-N single bond involving sp^2 hybridized C and N atoms [31]. In agreement with this assumption the amino groups are not pyramidal and the electron densities of the amino groups were found to be in plane with the 2-amino-5-chloropyridine skeleton.

In the complex, bifurcated intramolecular N1/N2-H…Cl2 hydrogen bonding are observed (Table 3). In spite of the fact that Cl atom is not a very good H-bond acceptor, the Cl…H distances are typical for such interactions [32]. Adjacent complexes are linked by a third N-H…Cl intermolecular interaction to form ribbons that in turn are connected in a three-dimensional network by a further C7-H…Cl2 weak interaction (Fig. 3, Table 3). The crystal robustness is enhanced also by a weak intermolecular π−π stacking interactions between neighboring aromatic rings are observed with a face-to-face distance of 3.936 Å [33] (Fig. 4).

Table 2. Selected geometric parameters (Å, º)

Zn1—N2	2.049 (3)	Zn1—Cl2	2.2303 (9)
Zn1—N1	2.062 (2)	Cl3—C4	1.733 (4)
Zn1—Cl1	2.2224 (9)	Cl4—C9	1.733 (4)
N2—Zn1—Cl2	111.20 (8)	N1—Zn1—Cl1	105.41 (8)
N2—Zn1—N1	102.30 (10)	N1—Zn1—Cl2	112.25 (7)
N2—Zn1—Cl1	106.24 (8)	Cl1—Zn1—Cl2	118.07 (4)

Table 3. Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N4—H⋯Cl2	0.90(2)	2.58(2)	3.438(5)	164(2)
N3—H⋯Cl2	0.88(4)	2.46(4)	3.267(3)	154(3)
N4-H⋯Cl1[i]	0.89(4)	2.49(4)	3.335(49	159(3)
C7—H7⋯Cl2[ii]	0.93	2.82	3.616(5)	143

Symmetry code: (i) x-1/2,3/2-y,z+1/2; (ii) x,y,z+1
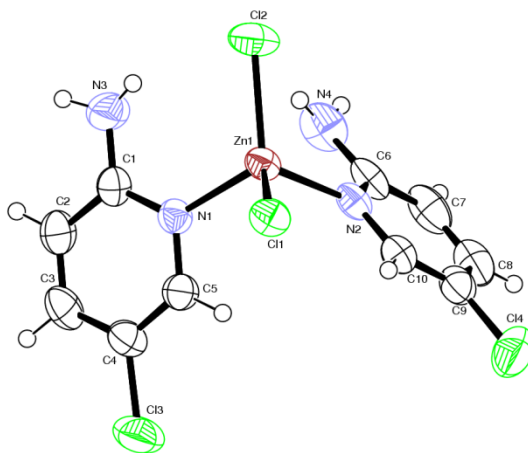
Figure. 1 Asymmetric unit of [ZnCl$_2$(C$_5$H$_5$ClN$_2$)$_2$] with the atom numbering scheme and thermal ellipsoids at 50 % probability.
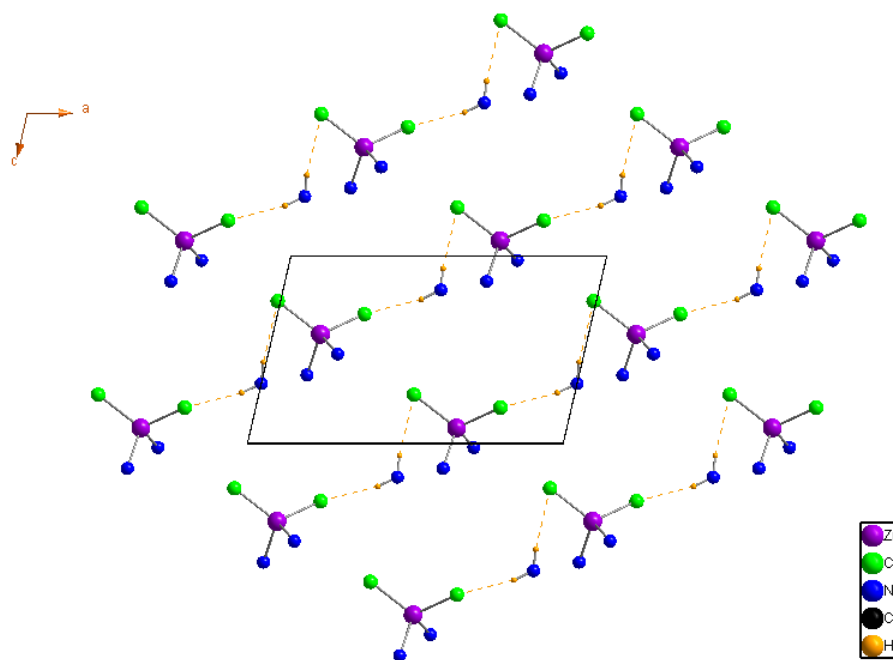
Figure. 2 [(ZnCl$_2$N$_2$)NH$_2$)]$_n$ chain in [ZnCl$_2$(C$_5$H$_5$ClN$_2$)$_2$]. The dotted lines indicate hydrogen bonds.
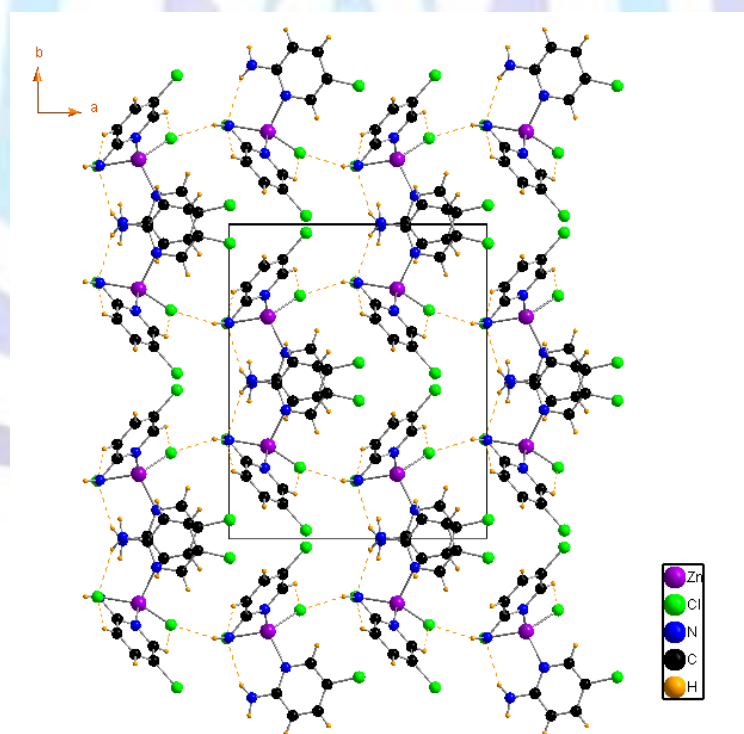
Figure. 3 Inorganic layer in [ZnCl$_2$(C$_5$H$_5$ClN$_2$)$_2$]. The dotted lines indicate hydrogen bonds.
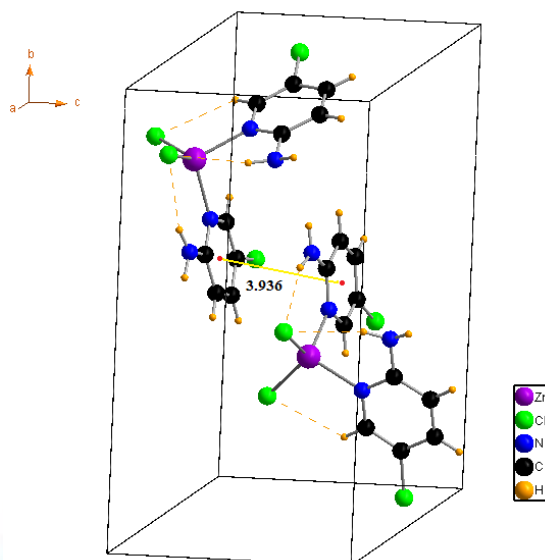
Figure. 4 π-π stacking interactions between neighboring aromatic rings in [ZnCl$_2$(C$_5$H$_5$ClN$_2$)$_2$].

3.2. NMR spectroscopy

The ^{13}C CP-MAS NMR spectrum of the title compound is shown on Figure 5. It displays seven well-defined resonances. The presence of a resonance peak number superior than five in this spectrum proves the existence of two crystallographically independent organic molecules in the asymmetric unit cell. This result is in good agreement with the X-ray data. 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 molecule depicted on Fig. 1. In all cases the theoretical chemical shifts were subtracted from that 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 the X-ray diffraction data give C-H or N-H distances which are too small compared to what is usually observed (typically below 0.1 nm) due to the fact that this method is not sensitive to the nuclei but to the electrons and so gives values corresponding to distances between the barycenters of electronic charges. As a consequence the positions of protons were first optimized, the C and N atoms being located at the positions given by the X-ray study. The resulting C-H and N-H distances correspond to what is usually obtained (typically 0.109 nm for C-H and 0.104 nm for N-H)

(3) Full optimization of all atoms and calculation of NMR chemical shifts. This calculation, compared to the above one can give indications on the steric hindrance around the organic cation and on the positions where it is the strongest. The atoms are labeled as depicted below:
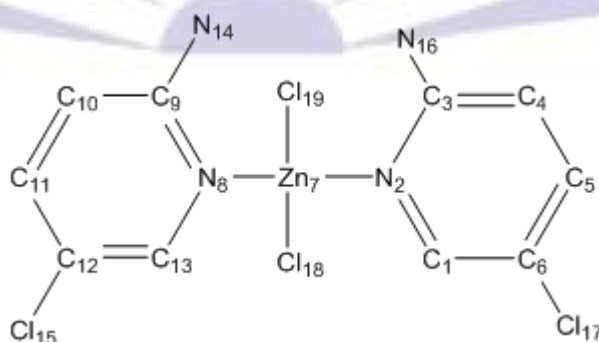
The results are listed in Table 4, while Figure 6 shows the correlation between experimental and calculated values (after optimization of the protons positions). Clearly, there is a good agreement between the experimental and theoretical values calculated after optimization of the position of the protons, allowing unambiguously the attribution of the different NMR signals.
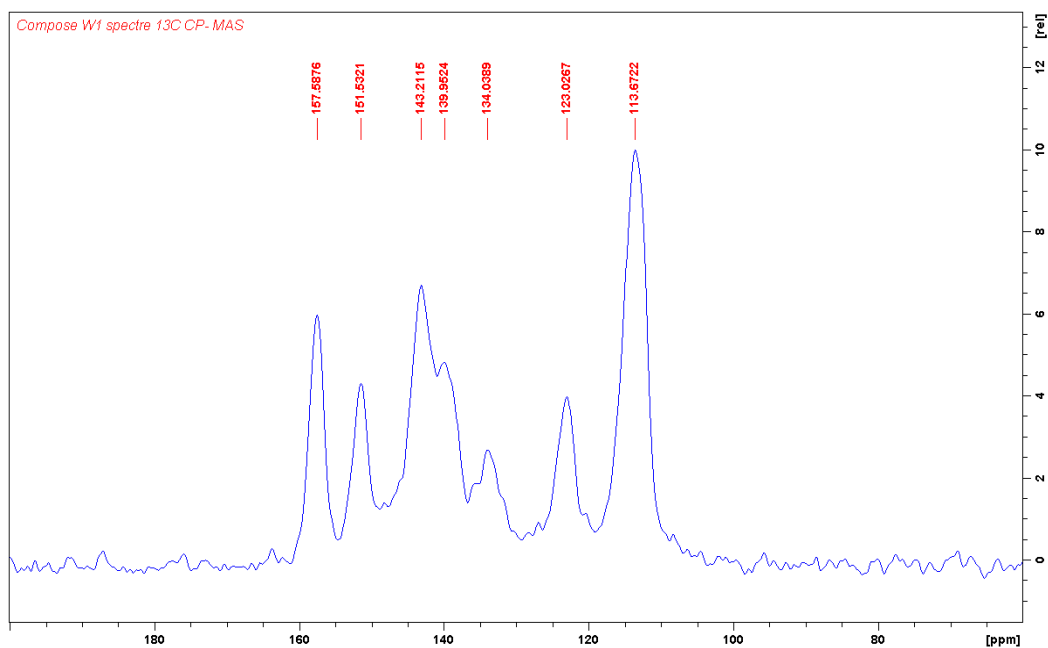
Figure. 6 ^{13}C CP-MAS NMR spectrum of [ZnCl$_2$(C$_5$H$_5$ClN$_2$)$_2$].

Table 4 . Chemical shift values of the carbon atoms in [ZnCl$_2$(C$_5$H$_5$ClN$_2$)$_2$].

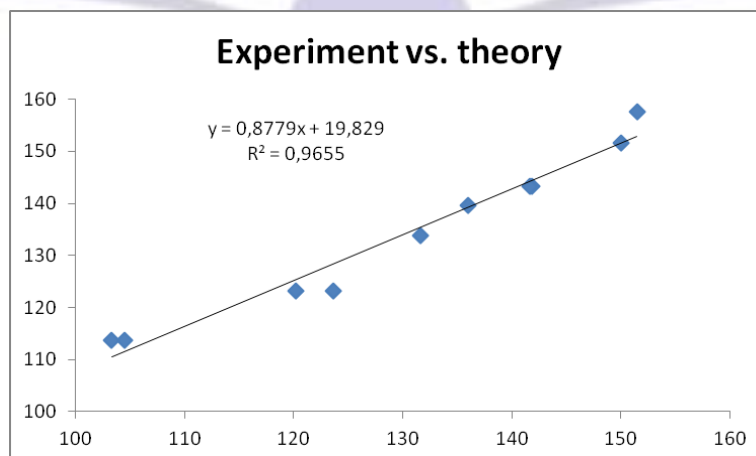| Carbon	X-rays	Full optimisation	Optimisation of protons	Experimental
C1	136.9	145	141.8	143.3
C3	152	154.4	151.5	157.7
C4	98	106.5	104.5	113.7
C5	130.4	136.6	136	139.6
C6	126.5	126.7	123.6	123.2
C9	149.9	154.1	150	151.7
C10	97.1	106.7	103.3	113.7
C11	126.1	136.1	131.6	133.9
C12	122.6	126.8	120.2	123.2
C13	137.1	144.8	141.7	143.3

Figure. 7 Comparison between experimental and calculated carbon-13 chemical shifts in [ZnCl$_2$(C$_5$H$_5$ClN$_2$)$_2$.

3.3 IR absorption spectroscopy

FTIR spectroscopy was used to verify the functional groups present in the crystal and their vibrational behavior in the solid state. Hydrogen bonding interactions are able to affect both frequency as well as intensity and width of the vibrations. The IR spectrum of crystalline $[ZnCl_2(C_5H_5ClN_2)_2]$ is shown in Figure 7. The most representative and characteristic vibrational modes of this compound can be compared to those of similar complexes [34-36]. In the high-frequency region, the broad bands between 3500 and 3000 cm^{-1} correspond to the valence vibrations of the C-H and N-H groups [37].The observed bands in the 1670-1100 cm^{-1} region can be attributed to the bending vibrations of the N-H groups and to the valence vibrations of the C=C double bonds of the aromatic ring and to the stretching and bonding modes $\square$ (GC), $\square$ (GN), $\square$ (GH) and groups [38, 39].The bands between 1000 and 600 cm^{-1} are assigned to the out of plane bending modes $\gamma(C_{ary}\text{-}H)$, $\gamma(C_{ary}\text{-}C_{ary})$, $\gamma(C_{ary}\text{-}N_{ary})$ and $\gamma(N\text{-}H)$ [40].

DFT calculations were undertaken in order to comfort these attributions. They were made in the same conditions than for the NMR study. When taking the positions of all atoms as given by the X-ray diffraction study, numerous imaginary frequencies were found with values reaching -1700 cm^{-1}. In the case of the full optimization of all nuclei, no imaginary frequency was found but as the optimization led to a symmetric molecule the number of bands was found to be lower than that expected from the experimental study. Only the calculation where only the positions of protons were optimized led to reliable results in terms of number and positions of the bands, even if four imaginary frequencies were found but with a low value (between -30 and -80 cm^{-1}). This discrepancy is probably related to both the errors in the positions of the atoms in the X-ray determination and to the fact that the surrounding of the Zn complex was not taken into account.

The resulting calculated IR spectrum is shown on Figure 8 and is very similar to the experimental spectrum allowing a good correlation between the experimental and theoretical data as shown on Figure 9. Thus, the precision is well-sufficient to assign the experimental frequencies and to confirm the attributions proposed above.
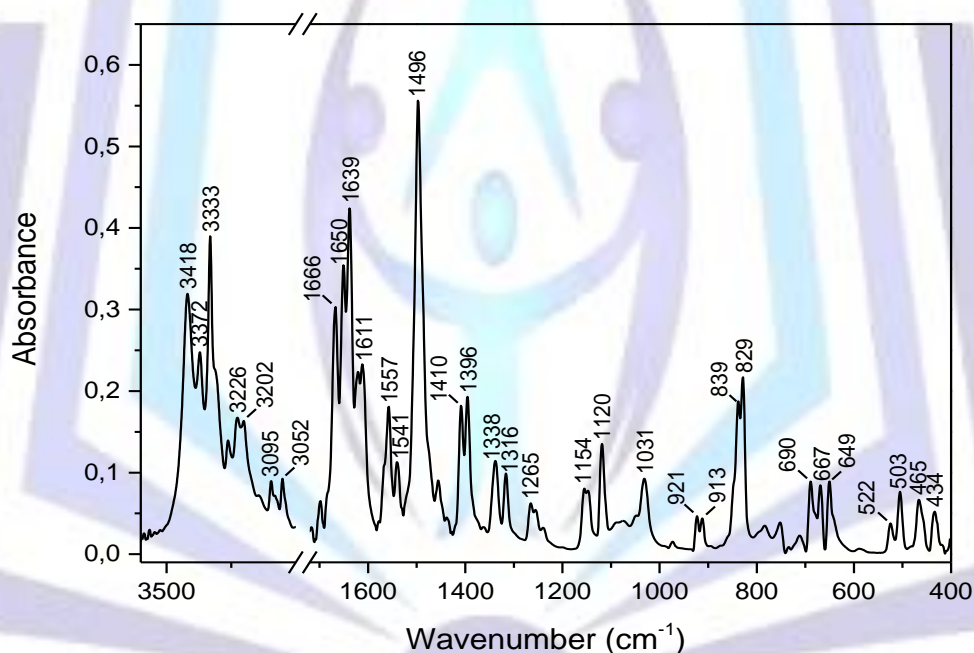

Figure. 8 IR absorption spectrum of $[ZnCl_2(C_5H_5ClN_2)_2]$.

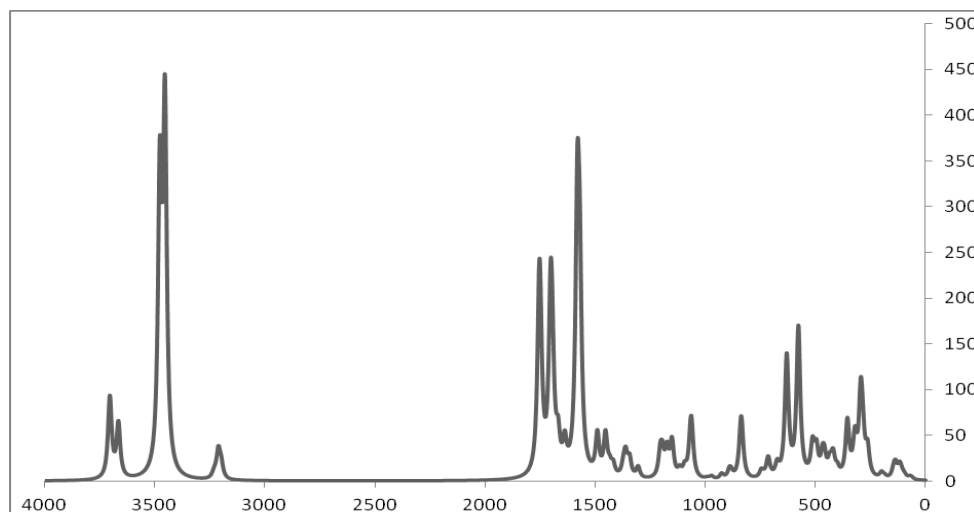**Figure. 9 Calculated IR absorption spectrum after optimization of protons of [ZnCl$_2$(C$_5$H$_5$ClN$_2$)$_2$.**
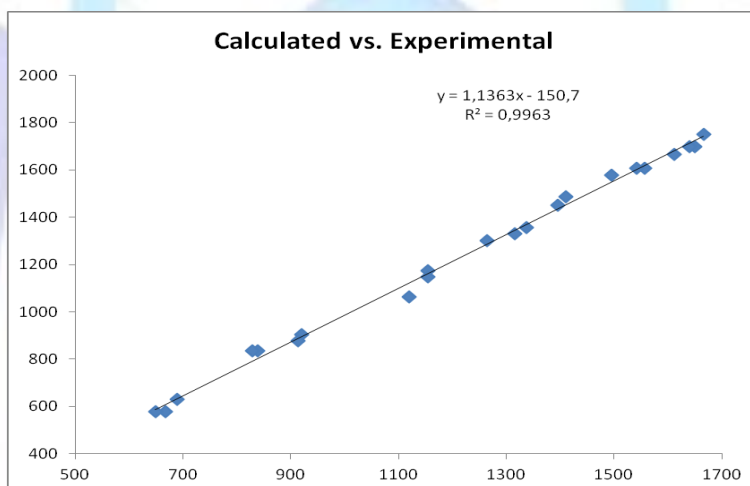

Figure. 9 Comparison between experimental and calculated IR frequencies.

3. Conclusion

A new noncentrosymmetric Zn(II) complex with the ligand 2-amino-5-chloropyridine has been prepared at room temperature. In the title compound, the organic entity behaves as a monodentate ligand and the metal center adopts a slighly distorted geometry. In the crystal structure, ZnCl$_2$N$_2$ tetrahedra are interconnected via N-H···Cl hydrogen bonds generated by the NH$_2$ amino group to form chains extending along the (*a-c*) direction. The crystal structure is stabilized by sets of intra- and intermolecular hydrogen bonds. Weak intermolecular □ □ □stacking interactions between neighboring aromatic rings contribute also to the structure cohesion. The number of ^{13}C CP-MAS NMR lines is in full agreement with the crystallographic data.

Acknowledgements

Supplementary data

CCDC 1017820 contains the supplementary crystallographic data for the title complex. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the CCDC, 12Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

References

[1] K. Bhar, S. Khan, J. S. Costa, J. Ribas, O. Roubeau, P. Mitra, B. K. Ghosh, Angew. Chem. Int. Ed. 51 (2012) 2142-2145.

[2] P. A. Vigato, S. Tamburini, Coord. Chem. Rev. 252 (2008) 1871-1995.

[3] C. R. Perez, J. G. Platas, H. Lotter, L. Lezama, X. Solans, S. Dominguez, P.M. Zarza, M. J. Rocio, M. S. Palacios, P. Gili, Inorg. Chim. Acta 255 (1997) 139-148.

[4] L. H. Uppadine, J.P. Gisselbrecht, J. M. Lehn, Chem. Commun. (2004) 718-719

[5] L. H. Uppadine, J. M. Lehn, Angew. Chem., Int. Ed. 43 (2004) 240-243.

[6] S. Banerjee, S. Mondal, S. Sen, S. Das, D. L. Hughes, C. Rizzoli, C. Desplanches, C. Mandal, S. Mitra, Dalton Trans. 4 (2009) 6849-6860.

[7] R. Gaur, L. Mishra, Inorg. Chem. 51 (2012) 3059-3070.

[8] J. Y. Lee, O. K Farha., J. Roberts, K. A. Scheidt, S. T. Nguyen, J. T. Hupp, Chem. Soc. Rev. 38 (2009) 1450-1459.

[9] D. P. Singh, D. S. Raghuvanshi, K. N. Singh, V. P. Singh, J. Mol. Catal. A: Chem. 379 (2013) 21-29.

[10] V. P Singh., K. Tiwari, M. Mishra, N. Srivastava, S. Saha, Sens. Actuators, B182 (2013) 546-554.

[11] A. Sahana, A. Banerjee, S. Das, S. Lohar, D. Karak, B. Sarkar, S. K. Mukhopadhyay, A. K. Mukherjee, D. Das, Org. Bio. Chem. 9 (2011) 5523- 5529.

[12] A.S. Fouda, M.M. Gouda, S. I. Abd El-Rahman, Bull. Korean Chem. Soc. 21 (2000) 1085-1089.

[13] R. R. Crichton, Biol. Inorg. Chem. 2 (2012) 69-89.

[14] R. Masse, M. Bagieu-Beucher, J. Pécaut, J. P. Levy, J. Zyss, Nonlinear. Opt. 5 (1993) 413-423.

[15] R. Masse, J. Zyss, Mol. Eng. 1 (1991) 141-152.

[16] J. Zyss, J. L. In Brédas, R. R. Chance, NATO-ASI Series, Series E: Applied Sciences,   182,   Kluwer Academic, Dordrecht, (1989) 545.

[17] A. Fkyerat, A. Guelzim, F Baert., W. Paulus, G. Heger, J. Zyss, A. Périgaud,

Acta Cryst. B51 (1995) 197-209.

[18] K. Kaabi, M. El Glaoui, M. Zeller, C. Ben Nasr, Acta Cryst., E66 (2010) m1145-m1154.

[19] R. H. Blessing, Acta Crystallogr., A51 (1995), 33-38

[20] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115-119

[21] H. D. Flack, Acta Cryst. A39 (1983) 876-881.

[22] G. M. Sheldrick: SHELXL97, Program for Crystal Structure Refinement (1997); University of Göttingen, Göttingen, Germany

[23] L. J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837-838

[24]   K. Brandenburg, DIAMOND version 2.0, (1998).

[25]   M. N. Burnett, and C.K. Johnson, ORTEPIII. Report ORNL-6895, 1996, Oak Ridge National Laboratory, Oak Ridge, Tennessee, USA

[26] K. Robinson, G. V. Gibbs, P.H. Ribbe, Science, 172 (1971) 567-570

[27] A. L. Beauchamp, Inorg. Chim. Acta (1984), 91, 33

[28] A. Lennartson, S.Olsson, J. Sundberg, M.Hakansson, Inorg. Chim. Acta (2010), 363, 257

[29] R. Novotna, Z. Travnicek, I. Popa, Inorg. Chim.Acta 363 (2010) 2071-2079.

[30] A. S. Wills, VaList, Program available from www.ccp14.ac.uk

[31] S. Shanmuga, S. Raj; H.-K. Fun; P.-S. Zhao; F.-F. Jian; L.-D. Lu, X.-J. Yang; Wang X., Acta Cryst. C56, (2000) 742-743.

[32] D.Y. Wang, J-L. Wang, D.W. Zhang, Z. T. Li , Science China Chemistry 55, (2012),   2018-2026 Abu-Shandi

[33] T. Dorn, C. Janiak, K., Cryst. Eng. Comm., 7 (2005) 633–641.

[34] N. L. Calve, F. Romain, M. H. Limage, A. Novak, J. Mol. Struct. 200(1989),, 131.

[35] H. J. Ratajczak, J. Mol. Struct., 3 (1969) 27.

[36] A. Navak, J. Mol. Struct., 217(1990),, 35.

[37] W. Smirani, C. Ben Nasr, M. Rzaigui, Mat. Res. Bull., 39 (2004) 1103.

[38] K. Kaabi, A. Rayes, C. Ben Nasr, M. Rzaigui, F. Lefebvre, Mat. Res. Bull., 38, (2003) 741.

[39] A. Oueslati, C. Ben Nasr, A. Durif, F. Lefebvre, Mat. Res. Bull., 40 (2005), 970.

[40] A. Oueslati, A. Rayes, C. Ben Nasr, F. Lefebvre, Mat. Res. Bull., 40 (2005) 1680.