Revue Roumaine de Chimie, **2008**, *53*(3), 169–175

STRUCTURE AND CHARACTERIZATION OF A NEW INORGANIC-ORGANIC HYBRID COMPLEX OF Zn(II) WITH 2-AMINO-4-METHYLPYRIDINE

I. Ben GHARBIA,[a] R. KEFI,[a] C. Ben NASR [a]* and A. DURIF [b]

[a] Laboratoire de chimie des Matériaux, Faculté des Sciences de Bizerte, 7021 Zarzouna, Tunisie.
[b] LEDSS, Bâtiment Chimie Recherche, BP53, 38041 Grenoble, Cedex 09, France.

Received May 14, 2007

The new inorganic-organic hybrid complex of Zn(II) with 2-amino-4-methylpyridine, $(C_6H_9N_2)_2ZnCl_4$, has been prepared and characterized by X-ray crystallography, thermal analysis and solid state NMR spectroscopy. The complex crystallizes in the triclinic space group $P\bar{1}$ with a minimal tetrahedral distortion of the $ZnCl_4^{2-}$ ion, a = 7.473(2)Å, b = 8.469(3) Å, c = 15.376(8) Å, α = 95.14(2)°, β = 91.15(2)°, γ = 68.99(2)°, V = 904.79(2)Å^3 , Z = 2. In this complex, hydrogen bonding and π-π interaction play crucial roles in forming interesting structural patterns. The two pyridinium cations are aligned with each other in a face-to-face manner of electron receiving to donating center. Solid state ^{13}C CP-MAS-NMR spectroscopy is in agreement with the X-ray structure.

INTRODUCTION

Organic-inorganic-hybrid metal halides have received extensive attention in recent years owing to their great fundamental and practical interest. The architecture of metal halides can be turned at the molecule level so as to possess unusual electronic properties, various components and potential applications in areas of molecular adsorption, catalysis, electromagnetism, and photochemistry.[1-8]

In recent years considerable research activity has been aimed toward generating new supramolecular entities having desired structural network by self-assembly of metal ions utilising their preference for different coordination geometry, choice of suitable ligands, and intermolecular interactions such as hydrogen bonding and π-π interaction.[9-13] In the present investigation we report the synthesis and crystal structure of a new organic-inorganic hybrid zinc chloride. Its characterization by ^{13}C CP MAS NMR spectroscopy is also reported.

RESULTS AND DISCUSSION

1. Structure description

Figure 1 shows the ORTEP [14] plot of the structure including the atoms labelling and their vibrational ellipsoids at 40 % probability. The structure consists of one 2-amino-4-methylpyridiniumm cation, one 4-methylpyridin-2-aminium cation and one tetrachlorozincate anion. These two kinds of cations were separately observed in pyridyl-2- methylammonium nitrate[15] and in bis(2-amino-5-methylpyridinium) tetrachlorzincate.[16] The protonation of the two nitrogen atoms can be explained by the similar basicity of these atoms. Intermolecular bond distances and angles around the Zn(II) center are presented in Table 2.

Structural determination shows that the title compound crystallizes in the triclinic space group $P\bar{1}$. Bond lengths and angles within the organic ions are normal and compared to those reported for the 2-amino-5-methylpyridinium ions[17] and the

* Corresponding author: cherif.beunarr@fsb.rnu.tn

$CuCl_4^{2-}$ and $CuBr_4^{2-}$ salts.[18] The atoms building each ring of the title compound have a good coplanarity and they form a conjugated plane with average deviation of 0.0044 Å for the pyridinium ring and 0.0064 Å for the pyridinic ring. Stacking interactions between organic cations can be seen along the b-direction (Fig. 3). The centroid-centroid distance between two adjacent organic rings is 3.659 Å, less than 3.8 Å, the maximum value accepted for π-π interactions.[19]

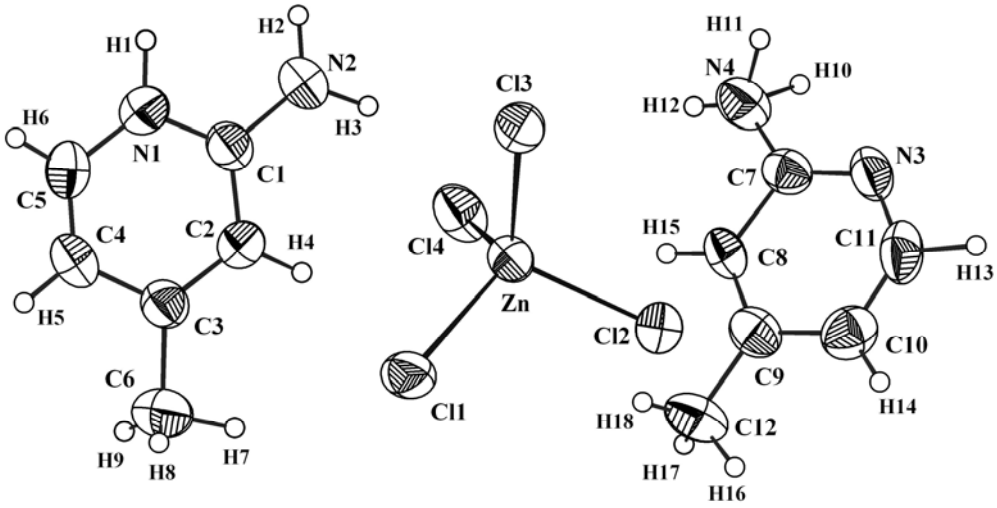

Fig. 1 – Asymmetric unit of $(C_6H_9N_2)_2ZnCl_4$. Thermal ellipsoids are shown at 40% probability.

Table 1

Crystal Data and Structure Refinement for $(C_6H_9N_2)_2ZnCl_4$

Crystal data	
Formula: C12H18Cl4N4Zn	F_w = 425.49 g.mol^{-1}
Crystal system : triclinic	Space group: P $\bar{1}$
a = 7.473(2), b = 8.469(3),	Z = 2
c = 15.376(8) Å	V = 904,7822 Å^3
α = 95.14(2), β = 91.15(2),	
γ = 68.99(2)°	
Refinement of unit cell	25 reflections
Parameters with:	(10< θ < 12°)
ρ_{cal} = 1.562 g.cm^{-3}	F(000) = 454
Linear absorption factor:	Crystal size (mm) : 0.4 x 0.2 x 0.3
μ (Mo K $\bar{\alpha}$) = 7.301 cm^{-1}	
Intensity measurements	
Temperature: 293 K	Wavelength: Cu K $\bar{\alpha}$ (1.5148 Å)
Diffractometer: Enraf-Nonius Mach3	Scan mode : □ / 2θ
Monochromator: graphite plate	Theta range: 5-74°
Measurement area ± h, ± k, l	h_{max} = 9, k_{max} = 10, l_{max} = 19
Nb of measured reflections:	3871
Nb of collected unique reflections:	3725 (Rint = 0.02)
Structure determination	
Program used: TeXsan [23]	
Determination:Direct methods SIR 92 [22]	
Unique reflections included:	1708 with I > 2 σ(I)
Residual Fourier density:	-0.58 < ρ < 0.83 e Å^{-3}
R = 0.0576 , wR = 0.0836	Refined parameters: 357
Largest shift error = 0.06	Esd = 2.12

Table 2

Selected Bond Lengths (Å) and Angles (deg) for $(C_6H_9N_2)_2ZnCl_4$

Bond length	Distance	Bond angle	Amplitude (deg)
Zn1─Cl1	2.262(1)	Cl4─Zn1─Cl1	112.71(4)
Zn1─Cl4	2.263(1)	Cl4─Zn1─Cl3	108.98(5)
Zn1─Cl3	2.269(1)	Cl1─Zn1─Cl3	109.44(5)
Zn1─Cl2	2.272(1)	Cl4─Zn1─Cl2	107.95(5)
N2─C7	1.328(5)	Cl1─Zn1─Cl2	107.33(4)
C7─N1	1.348(5)	Cl3─Zn1─Cl2	110.40(4)
N1─C18	1.350(6)	N2─C7─N1	118.6(4)
C18─C15	1.358(7)	C7─N1─C18	121.8(4)
C15─C14	1.421(7)	N1─C18─C15	121.9(4)
C14─C21	1.492(7)	C18─C15─C14	117.4(4)
C14─C22	1.364(6)	C15─C14─C22	120.1(4)
C22─C7	1.396(6)	C14─C22─C7	120.2(4)
N3─C12	1.328(5)	C22─C7─N1	118.6(4)
C12─C25	1.399(6)	C22─C7─N2	122.8(4)
C25─C17	1.363(5)	C21─C14─C22	121.3(4)
C17─C19	1.477(6)	C21─C14─C15	118.6(4)
C17─C10	1.402(6)	N3─C12─C25	120.5(4)
C10─C20	1.357(7)	C12─C25─C17	121.2(3)
C20─N4	1.372(6)	C25─C17─C10	118.7(4)
N4─C12	1.326(5)	C17─C10─C20	119.1(4)
		C10─C20─N4	120.7(4)
		C20─N4─C12	121.7(3)
		N4─C12─C25	118.5(3)
		N4─C12─N3	120.9(4)
		C19─C17─C10	120.4(4)
		C19─C17─C25	120.9(4)

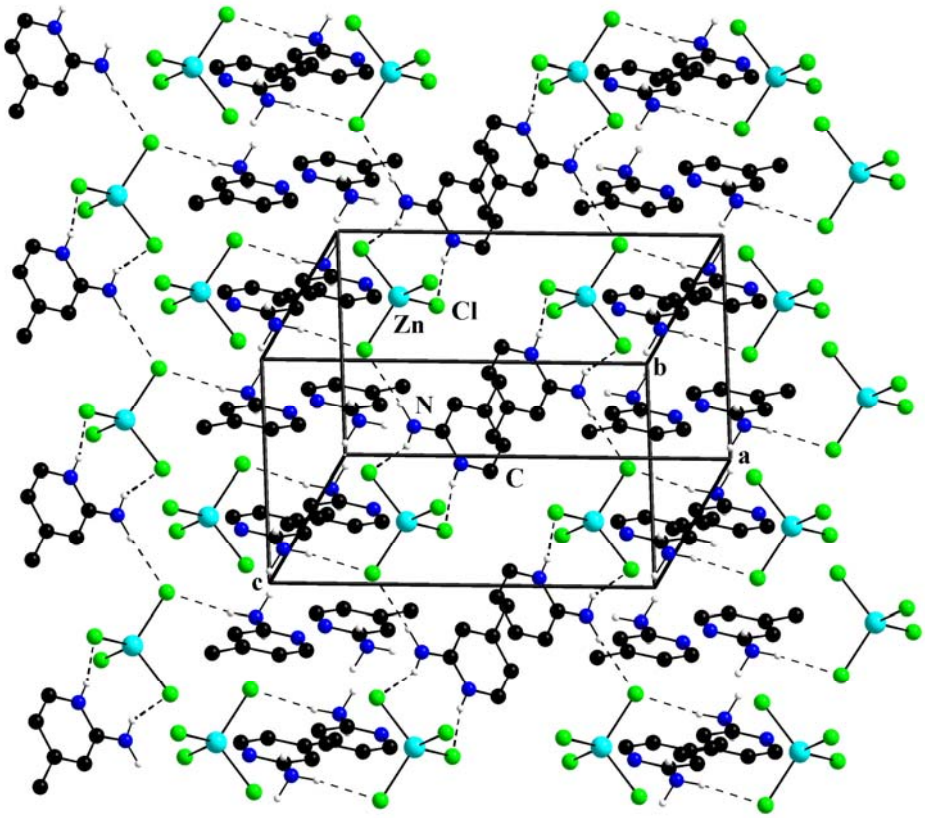

Fig. 2 – Packing diagram of $(C_6H_9N_2)_2ZnCl_4$ viewed parallel to the a-axis and showing the layer structure of the ions. All atoms are shown as spheres of arbitrary size and H atoms have been removed for clarity. Dashed lines represent D─A contacts from strong hydrogen bonds.

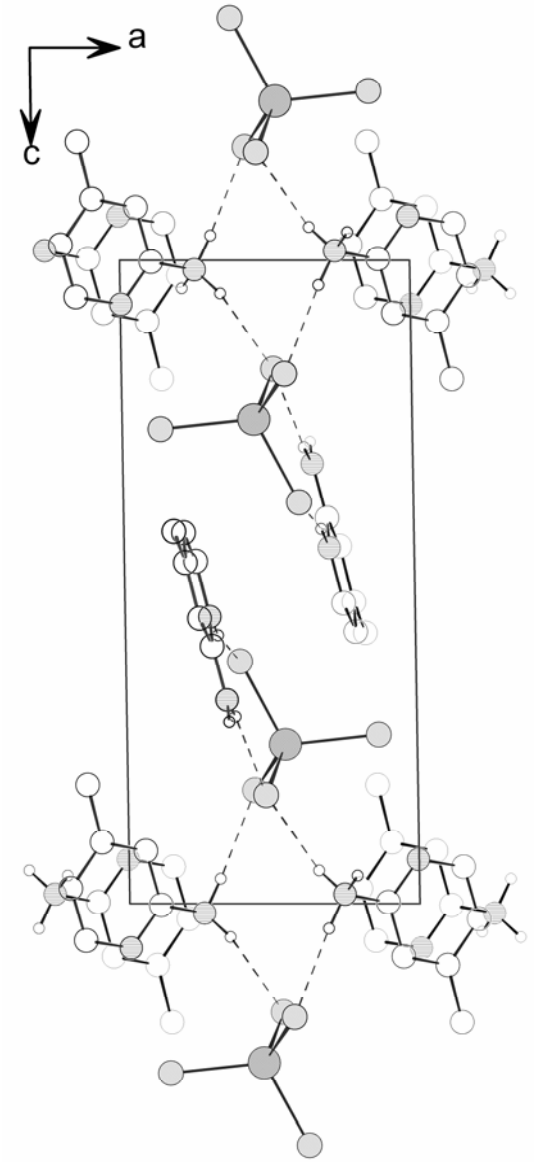

Fig. 3 – Projection of the structure of $(C_6H_9N_2)_2ZnCl_4$ along the b axis.

The atomic arrangement of the title compound can be described by ionic layers built up, with a repetition along the c direction, of superimposed rows of pyridinium rings followed by single rows of $ZnCl_4^{2-}$ anions (two different types of superimposed rows of cations are actually present, which are characterized by different stacking interactions) held together through four N-H…Cl hydrogen bondings. Among these latters, two are formed through the amine hydrogen atoms, one through the pyridine hydrogen atom and the remaining through amine protonated of the second independent 2-amino-4-methylpyridinium. Distances H…Cl vary between 2.17 and 2.45 Å. These values are smaller than the sum of the radii of Van Der Waals of the chlorine and hydrogen atoms ($r_{Cl} + r_H \leq 2.81$ Å); consequently these values correspond well to strong bonds. The pyridinium rings are incorporated into metal-based solid phases as ligand serving to buttress the organic layer.

As expected, the $ZnCl_4^{2-}$ anions are almost tetrahedral, unlike their CuX_4^{2-} counterparts,[20] with normal Zn-Cl bond lengths ranging from ~2.26 to 2.27 Å and angles from ~107.3 to 112.7°. Donor-acceptor distances for hydrogen bonds within the structure (see Table 3) are the same, within experimental error. Among the four chlorine atoms of the $ZnCl_4^{2-}$ anion, only Cl1, Cl2, and Cl3 are acting as acceptors of the hydrogen bonds. The Cl3 is the acceptor of two hydrogen bonds (N2-H36…Cl3, and N3-H38…Cl3). It is interesting to note that one Cl4 is not involved in hydrogen bonding. From the remaining two chlorine atoms, Cl1 and Cl2 are acceptors of single N1-H34…Cl1 and N2-H35…Cl2 hydrogen bonds, respectively.

In the $ZnCl_4$ tetrahedra, the mean values of Zn-Cl lengths and Cl-Zn-Cl angles [2.266 Å and 109.45°, respectively] are in agreement with those found in bis(2-amino-5-methylpyridinium) tetrachlorozincate [2.270 Å and 109.42°, respectively].[17] The $ZnCl_4^{2-}$ anion exhibits a small distorted tetrahedral geometry. Indeed, the Zn-Cl bond lengths do not differ appreciably with the shortest and longest bond lengths of 2.262(1) and 2.272(1) Å associated to Zn-Cl1 and Zn-Cl2, respectively, the Cl-Zn-Cl bond angles are also comparable, varying between 107.33(4) and 112.71(4)°, indicating a small deviation from perfect tetrahedral geometry around Zn(II), according to literature results,[17] in comparison to the tetrachlorocuprate salt [21]. Indeed, in this latter compound, the Cu-Cl bond lengths and Cl-Cu-Cl bond angles vary from 2.2166(7) to 2.2837(6) Å and from 94.75(2) to 138.95(3)°, respectively, indicating a large deviation from perfect tetrahedral geometry around Cu(II).

Table 3

Hydrogen bonds in $(C_6H_9N_2)_2ZnCl_4$

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N(1)-H(34)…Cl(1)	0.95	2.17	3.104(3)	169.0
N(2)-H(35)…Cl(2)	0.95	2.45	3.320(4)	152.5
N(2)-H(36)…Cl(3)	0.95	2.45	3.373(4)	164.7
N(3)-H(38)…Cl(3)	0.93	2.41	3.336(4)	172.8

2. NMR spectroscopy

The ^{13}C CP-MAS-NMR spectrum of crystalline organic-inorganic hybrid complex $[(C_6N_2H_9)_2ZnCl_4]$ is given in Fig.4. Whatever the experimental conditions (variable contact time, CP-MAS or simple high power decoupling) the spectrum shows only six resonances at 159.3, 154.0, 136.3, 116.0, 26.5 and 25.0 ppm while there are 12 independent carbon atoms in the unit cell.

If the attribution of the signals at 26.5 and 25.0 ppm to the two inequivalent methyl carbons is relatively easy and proves the presence of two organic molecules in the asymmetric unit cell, in good agreement with the X-ray structure, it is more difficult to attribute the other signals which are all due to the carbon atoms of the aromatic rings. These four peaks, with relative intensities close to 2:1:1:1 can be explained with only one organic molecule and so we can reasonably suspect from these results that the two different aromatic rings in the unit cell have very similar neighbouring due to the organic ligands stacking as described by X-ray structure.

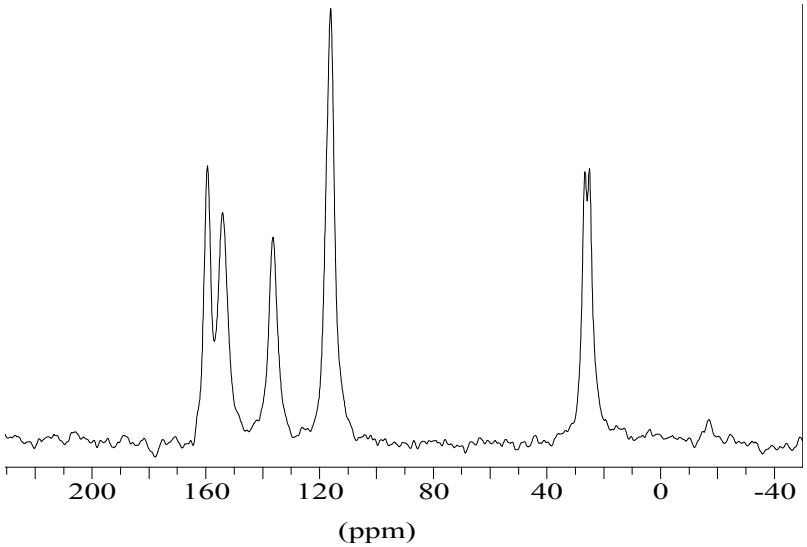

Fig. 4 – ^{13}C CP-MAS NMR spectrum of $(C_6H_9N_2)_2ZnCl_4$.

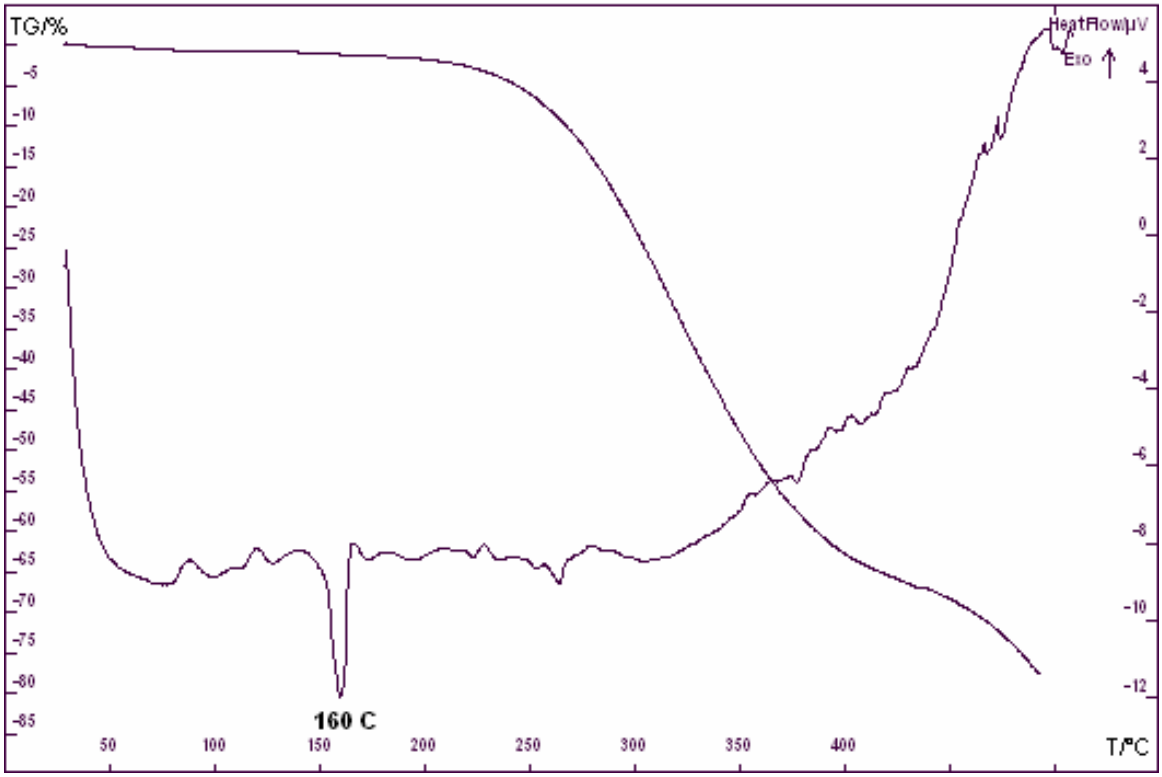

Fig. 5 – DTA and TGA curves of $(C_6H_9N_2)_2ZnCl_4$ at rising temperature.

3. Thermal analysis

Curves corresponding to DTA and TGA analysis, under argon flow are reported in Fig. 5. The DTA curve shows an endothermic peak at about 160°C, without weight loss. This peak can be attributed to a melting transformation confirmed by measure of melting point of the title complex. In the temperature range 200-500°C, the weight loss is 67.06 %, corresponding to the release of the organic groups and Cl_2. The whole weight loss (67.06 %) is in good agreement with the calculated value (67.18%).

EXPERIMENTAL

1. Chemical preparation

Crystals of the inorganic-organic hybrid complex of Zn(II) with 2-amino-4-methylpyridine, $(C_6H_9N_2)_2ZnCl_4$, were prepared by slow evaporation of an aqueous solution of 2-amino-4-methylpyridin, HCl, and $ZnCl_2$ (2:2:1). The crystals are stable for a long-time in normal conditions of temperature and humidity. The chemical formula was determined when resolving the crystal structure by X-ray diffraction spectroscopy.

2. Investigation techniques

The title compound has been studied by various physico-chemical methods: X-ray diffraction, solid state NMR spectroscopy and thermal analysis.

2.1. X-ray diffraction

The intensity data collection was performed using a MACH3 Enraf Nonius diffractometer. The experimental conditions of data collection, the strategy followed for the structure determination and the final results are given in Table 1. Selected bond lengths and angles are given in Table 2 and hydrogen-bonding data in Table 3.

The structure was solved by direct methods using the SIR92[22] program and refined by full matrix least-squares techniques based on *F* using teXsan[23]. The structure factors were obtained after Lorentz polarization corrections. The positions of the heavier atoms, including the Zn atom, were located by the direct method. The remaining atoms were found in a series of alternating difference Fourier maps and least-square refinements. The positions of the hydrogen atoms of this hybrid title compound were located directly from the difference Fourier maps. The drawings were made with Diamond[24].

2.2. NMR Spectroscopy

All NMR spectra were recorded on a Bruker DSX-300 spectrometer operating at 75.49 MHz for ^{13}C with a classical 4 mm probehead allowing spinning rates up to 10 kHz. ^{13}C NMR chemical shifts are given relative to tetramethylsilane (external references, precision 0.5 ppm). The carbon spectra were recorded by use of cross-polarization (CP) from protons (contact time 5 ms) and MAS. In all cases it was checked that there was a sufficient delay between the scans allowing a full relaxation of the nuclei.

2.3. Thermal behavior

Thermal analysis was performed using the "multimodule 92 Setaram" analyzer operating from room temperature up to 500 °C at an average heating rate of 5 °C.min^{-1}.

SUPPLEMENTARY MATERIAL

Crystallographic data for the title compound has been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC-266762). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223/336 033; mailto: deposit@ccdc.cam.ac.uk).

Acknowledgements: We would like to thank the Ministry of Scientific Research Technology and Competing Development of Tunisia for its financial support.

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