

PREPARATION AND CHARACTERIZATION OF ORGANIC-INORGANIC HYBRID CONTAINING MANGANESE (II) AND 4-AMINOPYRIDINIUM

Donia ZAOUALI ZGOLLI*, Habib BOUGHZALA, Ahmed DRISS

*Laboratoire de Matériaux et cristallographie, Faculté des Sciences de Tunis,
Université de Tunis El-Manar, 2092 El-Manar II, Tunis, Tunisie.*

(Reçu le 15 Octobre 2010, accepté le 12 Juillet 2011)

ABSTRACT: Organic-inorganic hybrid $\{(C_5H_7N_2)_2[MnCl_2(H_2O)_2]Cl_2\}_n$ was synthesized from ethanol solution containing manganese (II) chloride 4-hydrate and 4-aminopyridine under acidic conditions. The compound crystallizes in the monoclinic system, (space group $P2_1/c$) with $a=3.946(1)$ Å, $b=17.586(6)$ Å, $c=12.845(4)$ Å, $\beta=93.48(3)^\circ$, $V=889.7(5)$ Å³, $Z=2$, $R_w(F^2)=0.095$; $R(F^2)=0.036$. The link between organic and inorganic moieties is achieved by N-H...Cl and Cl...H-O hydrogen bonds. The electronic structure and thermal properties of the title compound were also studied by UV-vis, TGA, TDA, DSC, EDX and IR.

Keywords: Manganese; Organic-Inorganic Hybrid; 4-aminopyridine

RÉSUMÉ: Le matériau hybride organique-inorganique $\{(C_5H_7N_2)_2[MnCl_2(H_2O)_2]Cl_2\}_n$ sont préparés à partir d'un mélange stœchiométrique de $MnCl_2 \cdot 4H_2O$, $C_5H_6N_2$ et d'un excès d'acide chlorhydrique dans une solution d'éthanol. Le composé cristallise dans le système monoclinique (groupe d'espace $P2_1/c$) avec les paramètres de maille $a = 3,946(1)$ Å, $b = 17,586(6)$ Å, $c = 12,845(4)$ Å et $\beta = 93,48(3)$ Å. Sa structure a été résolue et affinée jusqu'aux facteurs de fiabilité non pondéré et pondéré $R_w(F^2) = 0,095$; $R(F^2) = 0,036$. La cohésion organique-inorganique est assurée par les liaisons hydrogène N-H...Cl et Cl...H-O. Ce composé a aussi été caractérisé par UV Visible, TGA, TDA, DSC, EDS et IR.

Mots clés : Manganèse ; hybride organique-inorganique, 4-aminopyridine

1. INTRODUCTION

For the past decades, organic-inorganic crystalline materials have inspired great interests for scientific study and device application because they combine properties of organic and inorganic compounds within one single molecular scale, such as second order nonlinear optical (NLO) response, magnetism, luminescence, and even multifunctional properties [1,2]. This kind of materials, generally expressed as $(R-NH_3)_2-MX_4$ or $(NH_3-R-NH_3) MX_4$ (where R: organic group, M: divalent metal and X: halogen) which can be regarded as a semiconductor/insulator multiple quantum well consisting of lead halide semiconductor layers sandwiched between organic ammonium insulator layers were prepared. [3,4].

In this paper, we report the synthesis, single crystal X-ray diffraction, IR, UV-vis, TDA, TGA, DSC and EDS studies of the organic-inorganic hybrid compound: $\{(C_5H_7N_2)_2[MnCl_2(H_2O)_2]Cl_2\}_n$.

2. EXPERIMENTAL

2.1. Synthesis

The title compound was prepared by the reaction of 4-aminopyridine dichloride, $C_5H_6N_2Cl_2$, with a stoichiometric amount of manganese chloride. Firstly, $MnCl_2 \cdot 4H_2O$ powder was added to the solution of $C_5H_6N_2Cl_2$ in anhydrous ethanol, the mixture was stirred for 2 hours; single crystals were obtained by slow evaporation of the solution at room temperature few days later.

* corresponding author, e-mail : donia_zgolli@hotmail.com

2.2. Characterization

2.2.1. Single crystal X-ray diffraction

The X-ray data collection was carried out on a prismatic crystal with an Enraf-Nonius CAD-4 diffractometer with Moka radiation graphite monochromated radiation Mo- $K\alpha$ ($\lambda=0.71069 \text{ \AA}$) at 293 K [5]. The Lorentz polarization effects, absorption via a psi-scan [6] and secondary extinction correction [7] were applied. The crystal structure was solved and refined in the monoclinic system (space group $P2_1/c$) to $R_w(F^2)=0.095$ and $R(F^2)=0.036$.

2.2.2. Physical characterization

IR spectra were recorded with samples in KBr pellets on a Bruker Vector 22 Fourier transform infrared spectrometer. UV-Vis absorption spectrum was obtained on a Varian Cary 100 Bio UV-vis spectrometer. Simultaneous thermogravimetric (TGA, TDA) and differential scanning calorimetric (DSC) analysis were performed on a SDT Q600 calorimeter from 20 to 250°C at the scanning rate of 5°C/min under nitrogen atmosphere. The EDX analysis was made on JEOL-JSM-5400 instrument.

3. RESULTS AND DISCUSSION

The different elements (C, N, O, Cl and Mn) in the complex are detected by the EDX on a scanning electron microscope (Fig 1).

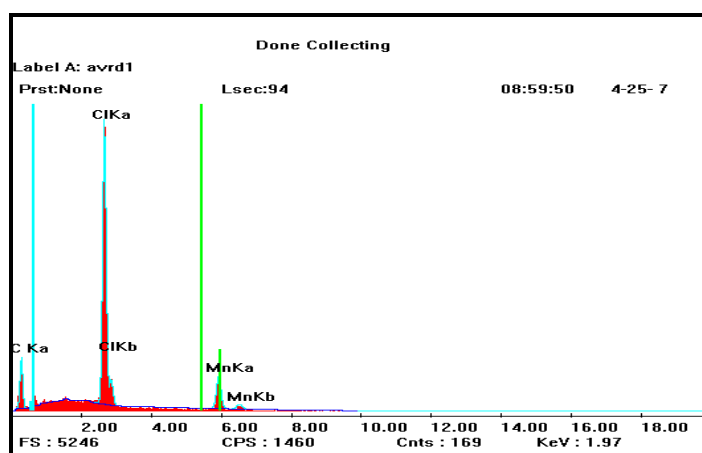


Fig 1: MEB curves of $\{(C_5H_7N_2)_2[MnCl_2(H_2O)_2]Cl_2\}_n$

3.1. X-ray crystal structure

A summary of the fundamental crystal data is given in Table 1. The cell parameters were determined and optimized by least-squares refinement based on 25 reflections in the range $9^\circ \leq \theta \leq 15^\circ$. The systematic absences as well as the statistical tests [8] in the reduced data indicated the inversion center and the space group $P2_1/c$ (table.1). The crystal structure was solved and refined using Full F^2 matrix least square. All calculations were performed using the SHELX-97 [7] computer

Table 1 Crystal and experimental data

$[MnCl_2(H_2O)_2] \cdot (C_5H_7N_2)_2 \cdot Cl_2$	421.01 g.mol ⁻¹
Monoclinic	$P2_1/c$
$a = 3.946 (1) \text{ \AA}$; $b = 17.586 (6) \text{ \AA}$; $c = 12.845 (4) \text{ \AA}$; $\beta = 93.48 (3)^\circ$	$V = 889.7 (5) \text{ \AA}^3$; $Z=2$
$F(000)=430$	$\mu = 1,35 \text{ mm}^{-1}$
Diffractometre	Enraf-Nonius CAD-4
T_{min} ; T_{max}	0,916 ; 0,999
Temperature	298(2) K
Correction d'absorption;	psi-scan ;
independent reflections	1892
reflections with $I > 2\sigma(I)$	1473
$[I > 2\sigma(I)]$; $wR(F^2)$	0,036; 0,095
$\Delta\rho_{min}$; $\Delta\rho_{max}$; ($e \cdot \text{\AA}^{-3}$)	-0,45 ; +0,38 ;
$S = 1.04$	112 parameters

programs included in the WinGX software package [9]. Molecular graphics are made with Diamond 2.1 [10].

The asymmetric unit contains a disordered organic cation (occupancies in the ratio 0.72:0.28), a chloride anion and an $[\text{MnCl}_4(\text{H}_2\text{O})_2]$ moiety with the MnII atom located on an inversion center. The structure is built up of infinite chains of edge-sharing $[\text{MnCl}_4(\text{H}_2\text{O})_2]$ octahedra developing parallel to the *a* axis which are separated by the 4-aminopyridinium ions and discrete chloride ions (Fig 2). The organic cations occupy the empty space around each inorganic chain. Structural cohesion is organized through N-H...Cl and O-H...Cl hydrogen bonds (Table 2), which build up a three-dimensional network [11].

Table 2 Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1—HW1...Cl1 ⁽ⁱ⁾	0,87	2,27	3,090 (2)	158
O1—HW2...Cl1 ⁽ⁱⁱ⁾	0,73	2,39	3,082 (2)	159
N1—H1A...Cl1	0,86	2,41	3,264 (4)	172
N1—H1B...Cl2	0,86	2,57	3,415 (4)	169
N1'—H1'1...Cl1 ⁽ⁱⁱⁱ⁾	0,86	2,47	3,30 (1)	163
N1'—H1'2...Cl1 ⁽ⁱ⁾	0,86	2,58	3,386 (9)	156

Symmetry codes: (i) $-x+1, 1/2+y, 3/2-z$; (ii) $-x, 1/2+y, 3/2-z$; (iii) $1+x, -y+1/2, z-1/2$

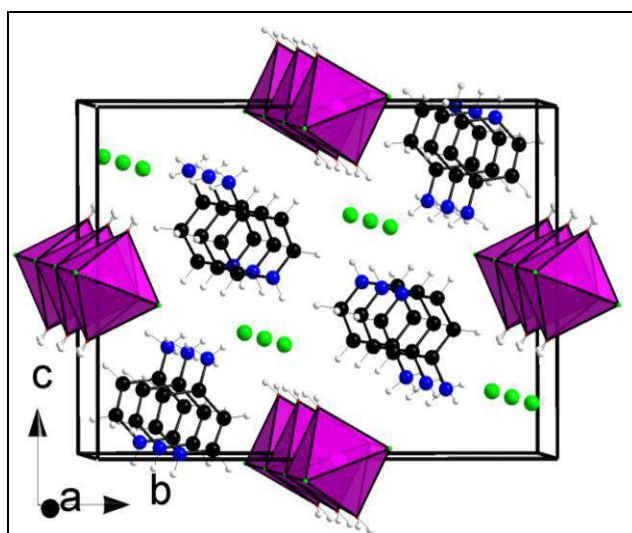


Fig 2: A projection of the title compound $\{(\text{C}_5\text{H}_7\text{N}_2)_2[\text{MnCl}_2(\text{H}_2\text{O})_2]\text{Cl}_2\}_n$ along the crystallographic *a*-axis.

3.2. IR

Fig 3 and Fig 4 show the IR spectra of $\text{C}_5\text{H}_6\text{N}_2$ and $\{(\text{C}_5\text{H}_7\text{N}_2)_2[\text{MnCl}_2(\text{H}_2\text{O})_2]\text{Cl}_2\}_n$ respectively. The stretching vibration peaks of $\nu(\text{NH})$ and $\delta(\text{NH})$ head groups of $(\text{C}_5\text{H}_6\text{N}_2)_2 \text{MnCl}_2 \cdot 2\text{H}_2\text{O} \cdot 2\text{HCl}$ shift to higher wave numbers (3320 and 1600 cm^{-1}) compared to that of $\text{C}_5\text{H}_6\text{N}_2$ (3300 and 1560 cm^{-1}). It indicates that N-H...Cl hydrogen bonds formed in the hybrid are weaker than that of 4-aminopyridine. The locations and the assignments for other peaks are $3400\text{-}3080 \text{ cm}^{-1}$ and $995\text{-}680 \text{ cm}^{-1}$ for water molecules.

The band at 1410 cm^{-1} and the broad bands between 2670 and 3080 cm^{-1} are attributed to the C–H stretching vibration. The weak bands at 3400 cm^{-1} and around 1600 cm^{-1} are due to N–H vibration

of 4-aminopyridine. The peak at 1190 cm^{-1} is likely due to the vibration of C–N [12,13]. The peak at 512 cm^{-1} can be attributed to Mn–Cl and Mn–O vibrations.

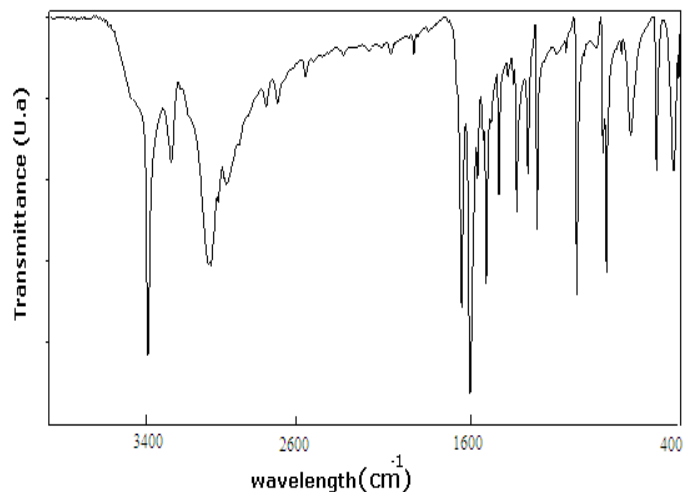


Fig 3: IR spectrum of $\text{C}_5\text{H}_6\text{N}_2$

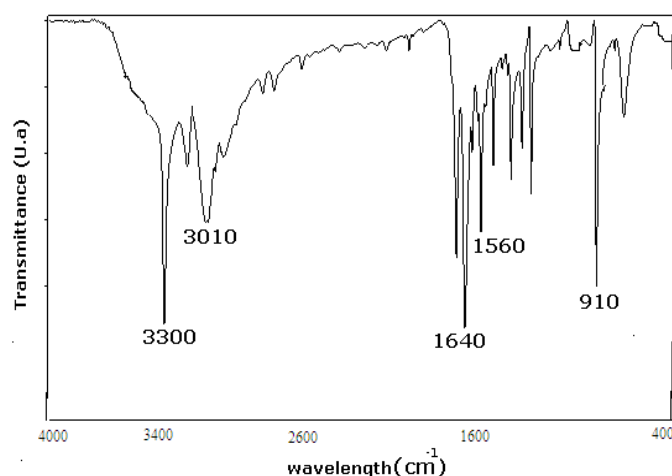


Fig 4: IR spectrum of $\{(\text{C}_5\text{H}_7\text{N}_2)_2[\text{MnCl}_2(\text{H}_2\text{O})_2]\text{Cl}_2\}_n$

3.3. Thermal analysis

DTA and TGA results are represented in Fig 5. Between 110°C and 130°C , the sum of the two-step loss converging to 9.5% is observed, probably corresponding to the departure of two chloride molecules per formula unit (calc. 8.5%). The DTA curve shows two endothermic peaks. Above 290°C and completed at 320°C , a second step loss is due to the departure of organic molecules, the observed weight loss of 52% is in good agreement with the calculated one of 49 % attributed to the evaporation of volatiles entities from the frameworks [14]. The state of the sample after experiment (black) suggests its decomposition.

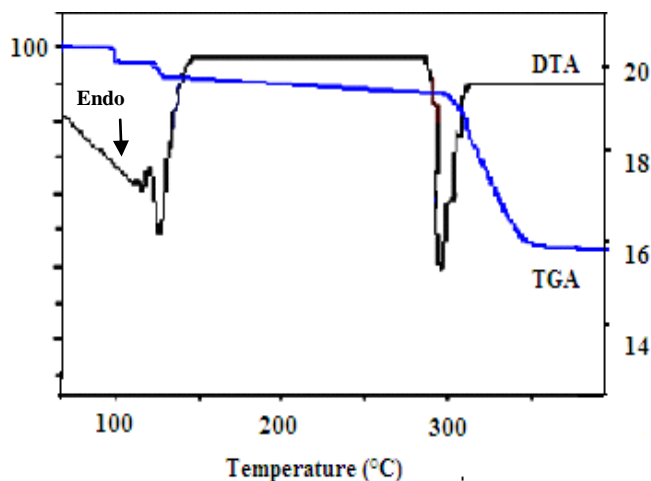


Fig 5: TGA and TDA curves of $\{(\text{C}_5\text{H}_7\text{N}_2)_2[\text{MnCl}_2(\text{H}_2\text{O})_2]\text{Cl}_2\}_n$

The DTA curve exhibits one weak endothermic peak at 300°C in comparison with the TGA curve, which corresponds to the organic molecules departure.

DSC studies on the title compound were undertaken demonstrating structural transitions below the melting decomposition point. In the DSC curve, one endothermic peak at 110°C corresponding to the decomposition of chloride, and its enthalpy is $\Delta H = 11.12 \text{ kJmol}^{-1}$ (Fig 6).

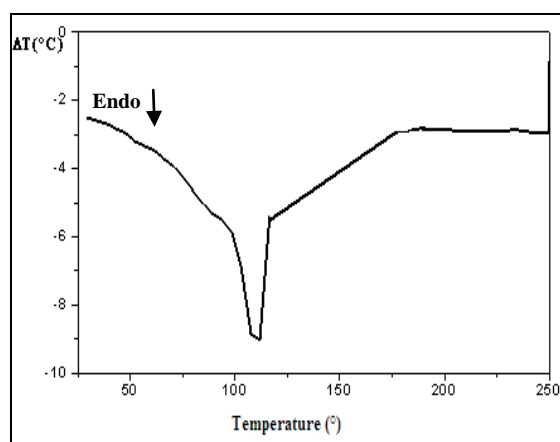


Fig 6: DSC curve of $\{(C_5H_7N_2)_2[MnCl_2(H_2O)_2]Cl_2\}_n$

3.4. UV-visible absorption spectra

Fig 7 shows UV-vis absorption spectrum of the $[MnCl_2(H_2O)_2] \cdot (C_5H_8N_2)_2 \cdot Cl_2$ measured at room temperature. This compound exhibits one distinct absorption band centred at 398 nm, which is similar to the previously reported organic-inorganic hybrid compound, such as manganese (II) complexes of 1,3-bis(2'-pyridylimino) isoindoline, $Mn(4R-ind)_2$ (R = H, Me) [15].

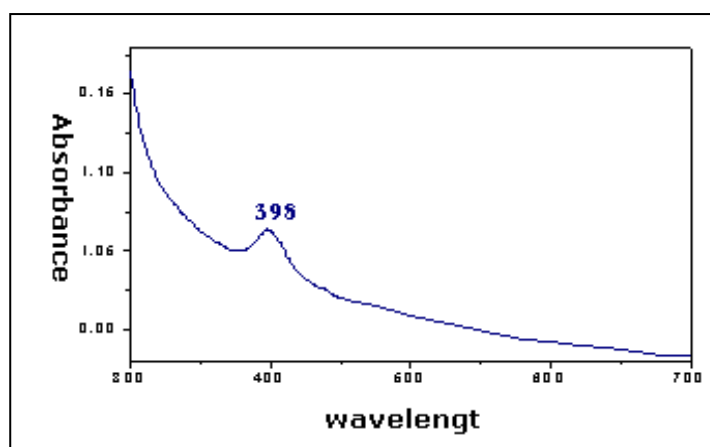
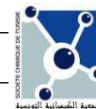


Fig 7: UV-Vis absorption spectrum of $\{(C_5H_7N_2)_2[MnCl_2(H_2O)_2]Cl_2\}_n$ measured at room temperature.

4. Conclusions

We have successfully synthesized $\{(C_5H_7N_2)_2[MnCl_2(H_2O)_2]Cl_2\}_n$ a novel organic-inorganic hybrid. Single crystal X-ray diffraction, IR, UV-vis, confirmed the formation of three-dimensional layered type structure. Further studies on its magnetic properties are underway.



References

- [1] D. B. Mitzi, *J. Chem. Soc., Dalton Trans.*, **2001**, 1-12.
- [2] P. G. Lacroix, R. Clément, K. Nakatani, J. A. Delaire, J. Zyss, I. Ledoux, *Science.*, **1994**, 263, 658-660.
- [3] J. Calabrese, N. L. Jones, R. L. Harlow, N. Herron, D. L. Thorn, Y. Wang. *J. Am. Chem. Soc.*, **1991**, 113, 2328-2330.
- [4] X. Hong, T. Ishihara, A. V. Nurmikko, *Solid State Commun.*, **1992**, 84, 657-661.
- [5] Enraf-Nonius. CAD-4 Express. Version 5.1/1.2-Enraf-Nonius, Delft, Netherlands., **1994**.
- [6] A.C.T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr.*, **1968**, A 24, 351-359.
- [7] G. M. Sheldrick, SHELXS-97 a Program for Crystal Structure Determination, University of Göttingen, Germany., **1997**.
- [8] R. E. Marsh, *Acta Cryst.*, **1995**, B51, 897-907.
- [9] L. J. Farrugia, *J. Appl. Crystallogr.*, **1999**, 32, 837-838.
- [10] DIAMOND - Visual Crystal Structure Information System CRYSTAL IMPACT, Postfach 1251, D-53002 Bonn.
- [11] D. Zouali Zgolli, H. Boughzala and A. Driss. *Acta Cryst.*, **2009**, E65, m921.
- [12] K. Nakamoto, *Infrared and Ramon Spectra of Inorganic and Coordination Compounds*, 3rd edition, Wiley Interscience, New York., **1978**.
- [13] P. Gütllich, A. Hauser, H. Spinger, *Angrew. Chem., Int. Ed. Engl.*, **1994**, 33, 2024-2054.
- [14] D. B. Mitzi, *Chem. Mater.*, **1996**, 8, 791-800.
- [15] J. Kaizer, G. Baráth, G. Speier, M. Réglie, M. Giorgi. *Inorganic chem commun.*, **2007**, issue 3, 292-294.