Journal of Asian Scientific Research, 2013, 3(5):454-461

Journal of Asian Scientific Research

journal homepage: http://aessweb.com/journal-detail.php?id=5003

PREPARATION, CRYSTAL STRUCTURE AND CARACTERIZATION OF INORGANIC-ORGANIC HYBRID PEROVSKITE $[NH_3\text{-}(CH_2)_{10}\text{-}NH_3]\ ZnCl_4$

K. ELMEBROUKI

Université Moulay Ismail, Laboratoire de Physique des Matériaux et Modélisation des Systèmes (LP2MS) associé au CNRST URAC08. Département de physique, Faculté des Sciences, Meknès, Maroc

M. KHECHOUBI

Université Moulay Ismail, Ecole Supérieur de Technologie. Route d'Agouray, Toulal, Meknès, Maroc

A. KAÏBA, A. BELAARAJ

Université Moulay Ismail, Laboratoire de Physique des Matériaux et Modélisation des Systèmes (LP2MS) associé au CNRST URAC08. Département de physique, Faculté des Sciences, Meknès, Maroc

D. MONDIEIGC, P. NEGRIER

Laboratoire Ondes et Matière d'Aquitaine, L.O.M.A, Université de Bordeaux I, cours de la libération Talence Cedex France

ABSTRACT

A new perovskite like system $[NH_3\text{-}(CH_2)_{10}\text{-}NH_3]\ ZnCl_4$, has been synthesized and characterized by single crystal X-ray diffraction, thermal analysis and infrared spectroscopic study. This compound crystallize in a triclinic space group P-1, with the unit cell parameters a=7.294(1), b=10.058(9) Å, c=12.812(1) Å, α = 90, 89(2), β = 101, 21(1), γ = 92, 40(3) and Z=2. The final R factor is 0,082. The structure of this compound might be described as layered with two parallel anionic and cationic layers. The first layer is composed by isolated distorted tetrahedral $(ZnCl_4)^{2-}$ and the second layer of $[NH_3\text{-}(CH_2)_x\text{-}NH_3]^{2+}$. Network hydrogen – bonding assures the cohesion between these layers and stabilizes the crystal. The structure shows the existence of a conformational disorder of the organic chains between « trans » and « twisted » states. The thermal analysis by DSC shows that the $2C_{10}ZnCl_4$ perovskite presents reversible phase transition.

Keywords: Perovskite structure, Molecular composite, X-ray diffraction, Crystal structure, Phase transitions in layered systems.

INTRODUCTION

In recent years, layered hybrid organic-inorganic compounds have attracted much attention due to their possibility to combine the properties of organic and inorganic materials at the molecular level (Day, P. and Ledsham, R.D.1982; Zangar, H. *et al.*, 1989). The class of hybrid materials is very large and proposes a wide set of different structures, properties and applications, in particular this material type can be used in solar energy storage (Busico, V. *et al.* 1977). The two dimensional perovskite layer family $[NH_3-(CH_2)_n-NH_3]MX_4$, n=2, 3,…, M=Mn, Fe, Cu, and Cd, X=Cl/Br, has intensively been investigated because of its reduced dimensionality and also because of the existence of numerous structural phase transitions (Mostafa, *M. F. et al.* 1997; Socfas, *C.et al.* 1980). The structure consists of infinite sheets made of corner-sharing octahedral MX_6. The cavities between the octahedron are occupied by the terminal NH_3 ends of the alkyl-chains, $[NH_3-(CH_2)_n-NH_3]$. They form N-H··· Cl hydrogen bonds with the chloride atoms of the octahedron (Kind, *R. et al.* 1979; Courseille *et al.* 1994). The sequence and nature of the structural phase transitions are functions of n, M and X. For short chains (n<5, order – disorder transitions of the alkylenediammonium chains are responsible for the phase transitions. In long chain materials as our case, conformational transitions as well as order-disorder phenomena of the chains exist. The compounds of which the organic chain contains a twisted conformation are suspected to present phases transitions (Khechoubi, M. 1993; Khechoubi, M. 2001). The conformations changes are reflected on the structural arrangement, in particular hydrogen bonds network. The compounds with Zn as metal present some difference compared with other of this series (Socfas, *C.et al.* 1980). Indeed, the inorganic layer is formed by un associated $[ZnCl_4]^{2-}$ tetrahedron in the place of two dimensional octahedron and is also known to have numerous structural phase transitions. We have chosen to investigate this type of materials: Because in the first, this materials exhibit a numerous solid state phase transition with suitable energy, in particular at room temperature (Socfas, *C. et al.* 1980; Mostafa *et al.* 2002; Wolthuis, Z. J *et al.* 1986). Moreover, they present magnetic, electric and optic prosperities because of their low dimensionality (Rubenacker, *G.V. et al.* 1985; Xu, C.Q. *et al.* 1991). The aim of this project; is to find materials having temperatures of transitions and energies suitable to use them as tank to store solar energy in the agricultural greenhouses and desalination of brackish water. In this work the $[NH_3-(CH_2)_{10}-NH_3]ZnCl_4$ ($2C_{10}Zn$) perovskite was synthesized and the structure was solved at room temperature. The thermal properties were determined by Deferential Scanning Calorimetric DSC.

EXPERIMENTAL PROCEDURE

Synthesis and Analysis

($C_{10}H_{26}N_2Cl_2$) is formed by adding an gaseous HCl to aqueous solution of $NH_2-(CH_2)_{10}-NH_2$ (gaseous HCl is obtained by adding drop by drop H_2SO_4 acid to solid NaCl)(Elmebrouki, K. *et al.* 2011).

Next, $C_{10}H_{26}Cl_4N_2Zn$ complex was prepared by mixing 1 M of an aqueous solution of ($C_{10}H_{26}N_2Cl_2$) with 1 M of an aqueous solutions of $ZnCl_2$.The solution acquired was clear, homogeneous and uncolored. The sample was left several days in dark room to obtain single crystals. Platelet crystals are formed.

The infra-red spectrum was recorded in the 400–4000 cm^{-1} range with a Perkin-Elmer FT-IR spectrometer using samples pressed in spectroscopically pure KBr pellets.

We used the Deferential Scanning Calorimetric DSC in a [293 – 120] K temperature range. Measurements were made on a sample of 10.5 mg, under nitrogen gas atmosphere with a speed of heaters of 5°C/min.

Crystallographic Studies

A single crystal of about 0.15 x 0.08 x 0.05 mm^3 was selected for diffraction experiments. The X-ray data collection was carried out on rotating anode Rigaku diffractometer R-axis four circle (using Cu Kα radiation (λ = 1.54180 Å). The collection data was made at room temperature using φ, ω scan mode, the crystal to detector distance was 40 mm, and further details are given in **Table1**. The structure was solved by SIR 97 (Altomare, A. *et al.* (1999).and the refinement of atomic parameters based on full – matrix least squares technique on F^2 were performed using the SHELX 97 (Sheldrick, G. M 1997). All non hydrogen atoms were refined anisotropically and all the hydrogen atoms were located theoretically. All the above programs were used within the WINGX package (Farrugia, L. J 1999). The molecular graphics were prepared using MERCURY program. The crystallographic Data of the structure described in this paper was deposited to the Cambridge crystallographic Data Center as supplementary publication No CCDC 929065

Table-1. Crystal data and structure refinement of 2C$_{10}$ZnCl$_4$

Data crystal	**2C$_{10}$Zn**
Empirical formula	$C_{10}H_{26}Cl_4N_2Zn$
Formula weight	381.50
Temperature	293(2) K
Wavelength	1.54180 Å
Crystal system	Triclinic
Space group	P-1
a	7.2940(1) Å
b	10.058(2). Å
c	12.8120(2) Å
α	90.89(2)°
β	101.210(2)°
γ	92.40(2)°
Volume	920.9(4) Å ^{3}
Z	2
Density (calculated)	1.376 Mg/m^3
Absorption coefficient	7.061 mm^{-1}
F(000)	396
Crystal size	0.15 x 0.08 x 0.05 mm^3
Theta range for data collection	3.52° to 69.95°.
Index ranges	$-8\leq h\leq 8, -12\leq k\leq 12, 0\leq l\leq 15$
Reflections collected	3480
Independent reflections	3480 [R(int) = 0.0000]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3480 / 0 / 154
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R_1 = 0.0828,wR_2 = 0.1679

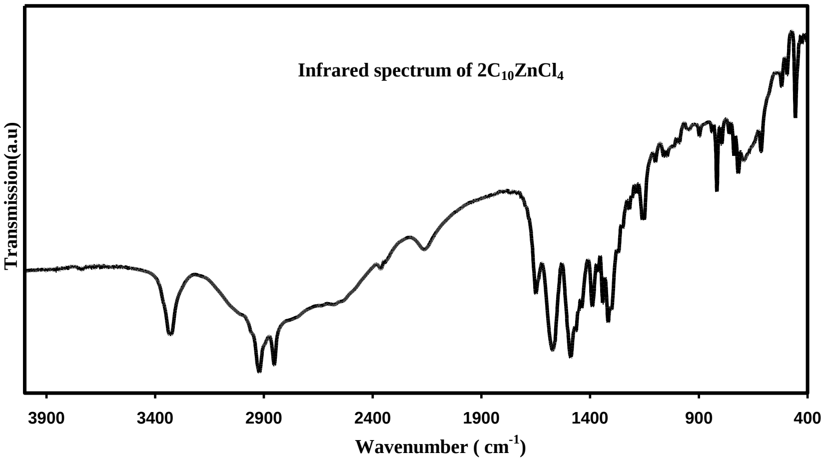
R indices (all data)	R_1 = 0.1878, wR_2 = 0.2346
Largest diff. peak and hole	0.609 and -0.690 e.Å^{-3}

RESULTS AND DISCUSSION

Vibrational Study

In order to give more information on the crystal structure, we have studied the vibrational properties using infrared absorption. **Fig1** show IR spectra of the $2C_{10}ZnCl_4$ at room temperature. The infrared spectra have been measured from 400 to 4000 cm^{-1}. A detailed assignment of the internal modes of the organic cations, observed of all the bands is difficult, but we can attribute some of them by comparison with the homologous compounds (Venkataraman, N. V. *et al.* 2002; Iskandar Chaabane *et al.* 2008).

Fig-1. Infrared spectrum of $2C_{10}ZnCl_4$.



The assignments of the bands observed in the infrared spectra are listed in **Table 2**. Indeed, the stretching vibration peaks of NH_3^+ groups shift to higher wave numbers lower than that of diamine. This can be attributed to the chemical environment change of NH_3^+ groups after the formation of perovskite system (Cheng, Z. Y. *et al.* (2003). The broad absorption bands in the 2500–3500 cm^{-1} range are due to NH_3^+ stretching modes.

Table-2. Frequencies of the observed Infrared bands of $2C_{10}Zn\ Cl_4$ proposed assignments

IR wave numbers (cm^{-1})	**$2C_{10}Zn$**
ν_{OH} (H_2O)	3540
ν_{as} (NH_3^+)	(3063, 2966)
ν_s (NH_3^+)	(2930 ; 2861)
ν_{as}(CH_2)	(2920, 2892, 2850)
ν_s(CH_2)	(2368, 2356, 2346)
δ_{as}(NH_3^+)	1586
δ_s(NH_3^+)	(1483, 1472)
δ_{Scis} (CH_2)	(1458 ; 1433)

$\delta_{\omega}(CH_2)$	(1402 ; 1387)
$\delta_{\tau}(CH_2)$	(1328 ; 1322)
ρ (NH_3^+)	1153
$\delta_{\tau}(NH_3^+)$	1076
$\nu_{C\text{-}N}$ (C-N)	1043
$\nu_{C\text{-}C}$ (C-C)	885
ρ (CH_2)	727
δ_{CCC} / δ_{CCN}	(536, 432, 416)

There is a well solved peak between 650 and 1600 cm^{-1}. It includes modes due to the symmetric bending of NH_3^+ group at 1489 cm^{-1} and asymmetric stretching of NH_3^+groupat 1583 cm^{-1}. The strong band at 825 cm^{-1} is associated to stretching mode of C–C–C. The vibration at 1058 cm^{-1} is due to the deformation mode of the NH_3^+ group. The band observed at 1073 cm^{-1} can be assigned to NH_3^+twisting mode and that at 1326 cm^{-1} to CH_2 twisting mode. The bands at 965 and 979 cm^{-1} are due to the C–N stretching. In the region less than 900 cm^{-1} frequency, there is presence of the C–N stretching bands as well as the C–C stretching bands. The bands located at 497 cm-1 and 446 cm^{-1} are attributed to the deformation of NCC angle in twisted conformation. The bands corresponding to the internal vibrational modes of the $(ZnCl_4^{2-})$ anion appear in the spectral region below 300 cm^{-1}. The C–N stretching bands are also known to shift the frequency positions of the progression bands above 900 cm^{-1}.A tentative assignment of wagging, rocking–twisting and twisting–rocking progression series were analyzed by assigning appropriate values from a comparison with the reported values for crystalline n-alkanes. (Venkataraman, N. V. *et al.* (2002). The infrared study confirms the presence of the organic part.

Single crystal X-ray diffraction

The crystallographic data, the measurements details and refinement are summarized in **Table1**. The compound crystallize in space group P_{-1}.The asymmetric unit cell consists of two half of organic chain with the other half is generated by inversion center and one tetrahedron$[ZnCl_4]^{2-}$ (**Fig 2)**. The title inorganic-organic hybrid compound contains two basic part, the unassociated $[ZnCl_4]^{2-}$ anion and the organic cation$^+H_3N(CH_2)_{10}NH_3^+$ (**Fig 3-a)**. Every organic chain has two protonated nitrogen atoms. The hydrogen bond assures the cohesion between organic and inorganic parts. So, the organic cation established ionic interactions and strong hydrogen bonds with $[ZnCl_4]^{2-}$ anions (N–H···Cl: 3.188(2) Å – 3.297(2) Å) to built infinite chains spreading along the **c** direction **(Fig 3-b**). The van der Waals contacts between these chains give rise to a three-dimensional network in the structure and add stability to this compound.

In the $[ZnCl_4]^{2-}$tetrahedra, the mean values of Zn—Cl bond lengths and Cl–Zn–Cl angles of 2.267Å and 109.5°, are in agreement with those found in the literature. The inorganic part is organized in sheets of isolated $[ZnCl_4]^{2-}$tetrahedra parallel to the (a; b) plane. Within these sheets, the nearest distances between neighbouring metallic sites are 5.798 Å, 6.467 Å and 7.294 Å. The atomic arrangement of the title compound can be described by inorganic layers organisation. The interlayer spacing is occupied by the organic molecules. The interlayer distance between two adjacent inorganic sheets is about 12.662 Å.

Fig-2. Asymmetric unit of $2C_{10}Zn\ Cl_4$ compound, at room temperature. Hydrogen atoms were omitted for clarity.

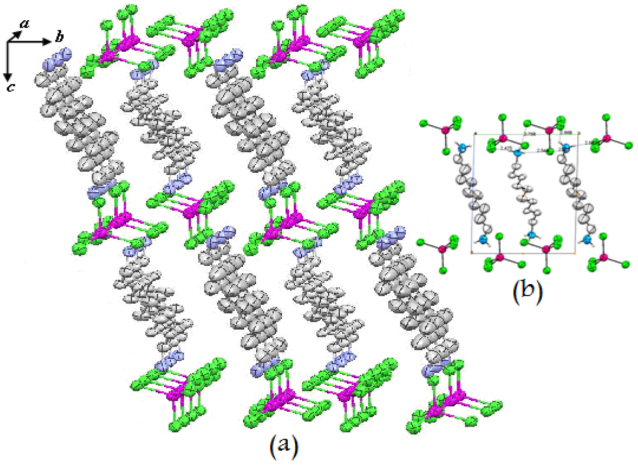
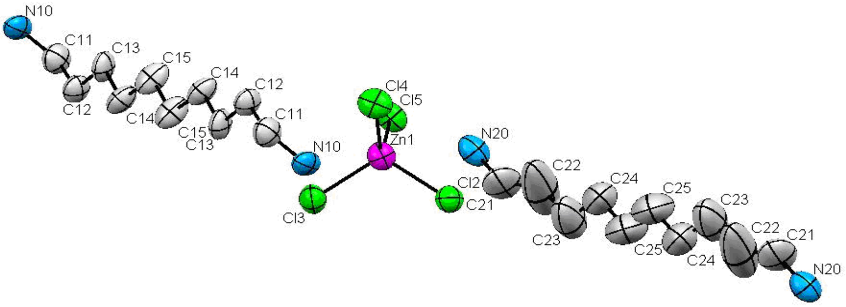


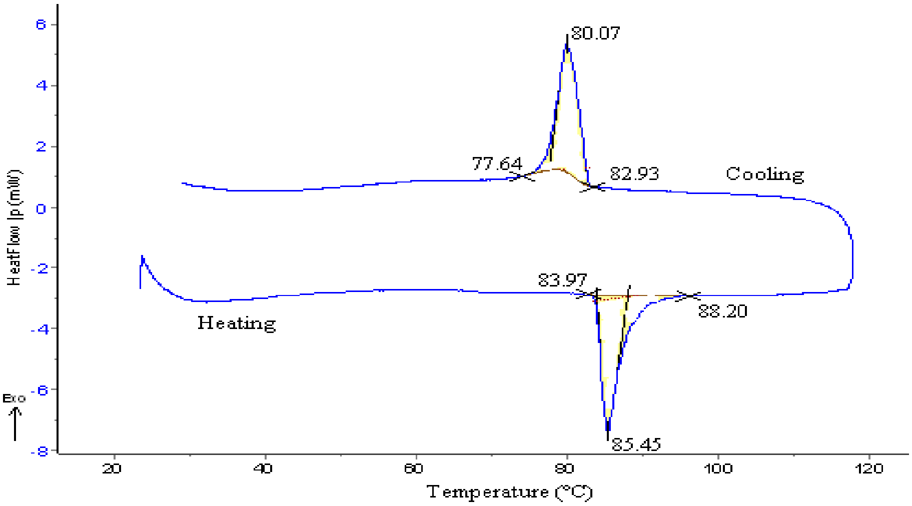
Fig-3. Packing diagram of $2C_{10}Zn\ Cl_4$ (a) viewed along the a-axis, **(b)** Projection of the structure along the a-axis. While Hydrogen atoms are omitted for clarity.



Thermal Analysis

Differential scanning calorimetry DSC measurements analysis was carried out to characterize the phase transitions of the inorganic-organic hybrid $2C_{10}ZnCl_4$, which is presented in **Fig4**. In the DSC curve, the endothermic transition at 85.45°C assigned to a solid – solid phase transition, and its enthalpy change is ΔH = 6.25 kJ mol^{-1}. The exothermic transition at 80.07 °C assigned to a solid – solid phase transition, and its enthalpy change is ΔH = 6.26 kJ mol^{-1}. Therefore, this compounds present reversible solid – solid phase transition, on the condition not exceeding melting temperature.

Fig-4. DSC curve of $2C_{10}ZnCl_4$



CONCLUSION

In summery, we have successfully synthesized an organic – inorganic hybrid like perovskite system, $[NH_3\text{-}(CH_2)_{10}\text{-}NH_3]\ ZnCl_4$, by using gaseous HCl. The results of Infrared spectroscopy and single crystal XDR measurement confirmed the formation of 0-dimensional (0)D layered perovskite type structure. The results of DSC measurement showed the presence of perfectly reversible solid - solid phase transition. Indeed this compound has the ability to store the energy. Further studies on its properties are underway

REFERENCES

Altomare, A., M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and J. R.Spagna., 1999. Appl. Crystallogr, 32: 115.

Busico, V., C. Carfagna, V. Salerno and M. Vacatello, 1977. The layer perovskites as thermal energy storage systems. Solar Energy, 24: 575-579.

Chaabane, I., H. Faouzi and G. Kamel, 2008. Synthesis, infra-red, raman, nmr and structural characterization by x-ray diffraction of $[C_{12}H_{17}N_2]_2CdCl_4$ and $[C_6H_{10}N_2]_2Cd_3Cl_{10}$ compounds. PMC Physics, B1: 11.

Cheng, Z.Y., Z. Wang, R.B. Xing, Y.C. Han and J. Lin, 2003. Chem. Phys. Lett. , 376: 481.

Courseille, C., N. Chanh, Th. Mars, A. Daoud, Y. Abid and M. Laguerre, 1994. Phys. Stat. Sol, 143a: 203.

Day, P. and R.D. Ledsham, 1982. Mol. Cryst. Liq. Cryst, 86: 163-174.

Depmeir, N., 1981. Acta cryst. B37: 330.

Elmebrouki, K., S. Tamsamani, J.Aazza, M. Khechoubi and A. Khmou, 2011. Synthesis and characterization of new materials like perovskite $[NH_3\text{-}(CH_2)_n\text{-}NH_3]ZnCl_4$ avec n=8 et 10. Journal of Asian Scientific Research, 1(3): 216-219.

Farrugia, L.J., 1999. J. Appl. Cryst, 32: 837.

Ishihara, T., J. Takahashi and T. Goto, 1990. Physical review B, 42: 11099-11107.

Khechoubi, M., 1993. Thèse de 3ème cycle. Université Bordeaux I, Bordeaux.

Khechoubi, M., 2001. Thèse d'etat. Université Moulay Ismail , Meknès.

Kind, R., S. Plesko, H. Arend, R. Blinc, B. Zeks, J. Selinger, B. Lozar., J. Slak, A. Levstik, C. Filipic, V. Zaga, G. Lahajnar, F. Milia and G. Chapuis, 1979. J. Chem. Phys, 71: 2118.

Mostafa, M.F., M.M. Abdelkader and S.S.A. Z., 2002. Naturforsch. 57a: 897-908.

Mostafa, M.F., R. Emrick and J. A. S. Atallah, 1997. App. . Phys. , 81: 4134.

Rubenacker, G.V., S. Waplak, S. L. Hutton, D. N. Haines and D.J.J. E., 1985. Applied physics 27: 3341-3342.

Sheldrick, G.M., 1997. Shelx97, program for the refinement of crystal structures. Germany: University of Göttingen.

Socfas, C., M. Arriendiaga, M. Tello, J. Fernandez and P. Gilli, 1980. Phys. Stat. Sol, 57a: 405.

Venkataraman, N.V., S. Barman, S. Vasudevan and Ram Seshadri, 2002. Structural analysis of alkyl chain conformation in the layered organic–inorganic hybrids $[C_nH_{2n+1}NH_3]_2PbI_4$ (n =12; 16; 18) by ir spectroscopy. . Chemical Physics Letters 358: 139-114.

Wolthuis, A.J., W. J. Huiskamp, L.J.D. jongh and R. Carlin., 1986. Physica 142b: 301.

Xu, C.Q., T. Kondo, H. Sakakura, Y. Takahashi and R. Ito., 1991. Solid state communications. 79: 245-248.

Zangar, H., Miane J. L., Courseille C., Chanh N. B., C. M. and M. Y., 1989. Phys. Stat. Sol, A115: 107.