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Molecular structure, experimental and theoretical spectroscopic characterization and non-linear optical properties studies of a new non-centrosymmetric hybrid material☆

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ABSTRACT

This paper gathers the synthesis and study of a novel nonlinear organic-inorganic (1,2-diammoniumcyclohexane tetrabromozincate (II) monohydrate; $[C_6H_{10}(NH_3)_2]ZnBr_4 \cdot H_2O$) hybrid. The newly developed hybrid was characterized by XRD and spectroscopic (FT-IR, Raman, UV–Visible and CP/MAS-NMR) studies. All theoretical calculations and structural optimization parameters were conducted by using DFT approach with B3LYP/6-31G(d) basis set and the vibrational wavenumbers were evaluated for the affectation of $[C_6H_{10}(NH_3)_2]ZnBr_4 \cdot H_2O$ compound by using transferable scale factor. The inspection of intermolecular links in the studied framework has been executed by the Hirshfeld surface analysis. The nonlinear optical characteristics of this compound were theoretically explored also the molecular orbitals (HOMO) and (LUMO) properties are performed to describe the charge transfer within the crystal.

1. Introduction

Nowadays, much consideration was provided to the Non-linear optical materials, which are the main focus of many research works going on around the world. They are very important related to their multiple applications in the several fields [1–4]. In this regard, an enormous part of hybrid materials have been investigated and developed to give a very great NLO ability. While the inorganic materials are known for their stability, the organic products are famous for their higher non-linear response. Thus, attempts to find out the benefits of the mixed organic and inorganic components having a non-centrosymmetric cell, and large nonlinear optical coefficients [5–9].

The hybrid compounds based on zinc halide attracts the interests of chemists for their photo-luminescent properties [10,11] and their structural flexibility. It is well-known that the structural chemistry of Zn (II) has demonstrated a propensity for forming a great diversity of geometries and range of coordination numbers [12–15].

It is interesting to prepare a novel organic inorganic hybrid compounds and to explore their structural characteristics and various properties. In previous research works [16–19] on hybrid compounds containing metal (II) halide anions with 1,2-diammonuimcyclohexane substituted cations have been studied and their attractive properties have been displayed.

In this investigation, a complete elucidation of the molecular geometry and vibrational spectral investigations of the crystal have been shown. Frontier molecular orbital (FMO) and Non linear optical properties for the title compound using the B3LYP/6-31G(d) level of theory were studied to elucidate information regarding charge transfer within HOMO–LUMO of the crystal.

2. Methodology

2.1. Experimental details

All reagents as well the solvents used were acquired from commercial suppliers and employed without further purification

☆ This work is a part of our project dealing with the physicochemical analysis and Non Linear Optical properties.

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unless.

The spectroscopic analyses of the of $[C_6H_{10}(NH_3)_2]ZnBr_4 \cdot H_2O$ compound are performed as reported the following; the FT-IR measurements were performed by the classical methods (KBr pellet of the samples) and using Nicolet Impact 410 FT-IR″ spectrometer in the 4000-400 cm^{-1}region. Concerning Raman scattering, it is developed at room temperature and recorded between 4000 and 50 cm^{-1} employing "LABRAMHR 800" triple monochromator instrument. The UV–Vis data was registered between 200 and 400 nm using Hitachi model U-3300 spectrometer. The CP/MAS-NMR measurements were evaluated under ambient conditions on a "Bruker MSL 300" spectrometer running at 75.48 MHz for ^{13}C and the simulation of the spectrum was achieved employing Bruker WINFIT software [20].

The X-ray Data were accomplished at 296 (K) on a BruKer AXS CCD four circle diffractometer outfitted with MoKα radiation (λ = 0.7073 Å), all reflections were executed from the WINGX program [21]. The structure was solved by the Patterson methods, using the SHELXS-97 [22] and refined with an independent atomic model against F^2 with SHELXL-97 [23] programs. All information concerning structure data and the details of the refinement are illustrated in Table 1. The molecular drawings were generated utilizing ORTEP [24] and DIAMOND programs [25].

2.2. Synthesis and crystal growth

The culture of $[C_6H_{10}(NH_3)_2]ZnBr_4 \cdot H_2O$ compound was conducted in two steps. At first, a batch of seed material was the preparation of 1,2-diammoniumcyclohexane bromide ($[C_6H_{10}(NH_3)_2]^{2+}$, $2Br^{-}$) by the mixture of an aqueous solution of 38% HBr (8 ml) with 1,2-diaminocyclohexane. The dried precipitates were then washed with diethyl ether in order to remove unreacted substances.

Second, the stoichiometric 1:1 amounts of ($[C_6H_{10}(NH_3)_2]^{2+}$, $2Br^{-}$) and $ZnBr_2$ were mixed and stirred for some minutes. The reaction occurred in the company of minimum volume of hydrobromic acid (HBr) and water. The solution was gradually evaporated at room temperature, the product isolated after approximately one week of growth and subjected to X-ray diffraction analysis.

2.3. Computational methods

The molecular Hirshfeld surfaces calculations [26–28], their associated two-dimensional fingerprint plots [29] and the Crystal Voids are performed using Crystal Explorer 3.0 [30].

It is a utilitarian tool to determine the intermolecular interactions and their quantitative contributions [31–33]. In this study, the Hirshfeld surfaces were constructed and the fingerprint maps were plotted as a function of both distances (d_e, d_i) which are explained by d_i, the distance from the point to the nearest atom and

Table 1
Crystal data and structure refinement for $[C_6H_{10}(NH_3)_2]ZnBr_4 \cdot H_2O$ crystal.

Crystal data	
Empirical formula	$[C_6H_{10}(NH_3)_2]ZnBr_4 \cdot H_2O$
Formula weight	519 (g/mol)
Crystal system	Orthorhombic
Space group	$Pna2_1$
Hall symbol	P 2c −2n P
Unit cell dimensions	
a (Å)	13.0317(5)
b (Å)	9.3398(4)
c (Å)	12.0334(5)
Volume (A^3)	1464.63(10)
Z	4
ρ calc (mg m^{-3})	2.35
Absorption coefficient (mm^{-1})	12.56
F(000)	984
Crystal dimensions (mm)	0.37 × 0.18 × 0.15
Crystal color	Prism, colorless
θRange for data collection (°)	1.0–25.38
Data collection	
Reflections collected	15279
Independent reflections	2695
Reflections with I > 2σ(I)	2528
Limiting indices	$h = -15 \rightarrow 15$ $k = -11 \rightarrow 11$ $l = -14 \rightarrow 14$
Absorption correction:	multi-scan (North, Phillips & Mathews (1968)) $T_{min} = 0.080$ $T_{max} = 0.154$
Refinement	
Refinement method	Full-matrix least–Squares on F^2
R [$F^2 > 2r(F^2)$]	0.025
w$R(F^2)$	0.065
Goodness-of-fit on F^2	S = 1.055
Extinction coefficient	0.0013(2)
$\Delta\rho_{max}$ (eÁ$^{-3}$)	0.001
$\Delta\rho_{min}$ (eÁ$^{-3}$)	0.000
CCD area detector diffractometer radiation source: fine-focus sealed tube Graphite ϕ and ω scans	976890

Primary atom site location: structure-invariant direct methods; Secondary atom site location: difference Fourier map. Hydrogen site location: inferred from neighboring sites H-atom parameters constrained.
$w = 1/[\sigma^2 (Fo^2) + (0.0247P)\ 2 + 4.8948P]$ where $P = (Fo^2 + 2Fc^2)/3$.