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Synthesis, Hirshfeld surface analysis, laser damage threshold, third-order nonlinear optical property and DFT computation studies of Dichlorobis(DL-valine)zinc(II): A spectroscopic approach

S. Chitrambalam [a], D. Manimaran [a], I. Hubert Joe [a, *], V.K. Rastogi [b], Israr Ul Hassan [c]

[a] Centre for Molecular and Biophysics Research, Mar Ivanios College, Thiruvananthapuram, 695 015, Kerala, India
[b] Indian Spectroscopy Society, KC 68/1, Old Kavinagar, Ghaziabad, 201 002, India
[c] Department of Mathematics and Sciences, College of Arts and Applied Sciences, Dhofar University, P.O. Box 2509, PC 211, Salalah, Oman

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ABSTRACT

The organometallic crystal of Dichlorobis(DL-valine)zinc(II) was grown by solution growth method. The computed structural geometry, vibrational wavenumbers and UV–visible spectra were compared with experimental results. Hirshfeld surface map was used to locate electron density and the fingerprint plots percentages are responsible for the stabilization of intermolecular interactions in molecular crystal. The second-order hyperpolarizability value of the molecule was also calculated at density functional theory method. The surface resistance and third-order nonlinear optical property of the crystal were studied by laser induced surface damage threshold and Z-scan techniques, respectively using Nd:YAG laser with wavelength 532 nm. The open aperture result exhibits the reverse saturation absorption, which indicate that this material has potential candidate for optical limiting and optoelectronic applications.

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1. Introduction

Nonlinear optical (NLO) properties of organometallic compounds are considerable interest because of their applications in telecommunication, image processing, data storage, optical modulation, optical switching and optical limiting [1,2]. A large number of organometallic complexes with efficient NLO properties have been synthesized and studied over the past thirty years [2–6]. The metal-ligand binding interactions plays an important role in increasing their NLO efficiency of the organometallic compounds. The nonlinear response in transition metal-organic compound may be due to the combinations of central metal and ligand as well as the charge transfer nature of the metal to ligand coordination bonds [7]. Therefore, transition metal-ligand coordination has been expected to be one of the new candidates for nonlinear optical materials, and it has been found that metal-ligand coordination exhibits good third-order NLO effects. Several papers have reported the NLO responses in the transition metal cluster family including optical absorption coefficient (β), refractive index (n_2), susceptibility ($\chi^{(3)}$), second-order hyperpolarizability (γ) and optical limiting effects [8–12]. Recently, crystal growth combination of amino acid with a transition metal compound has been proposed as a new candidate for NLO applications [13–16]. The crystal structure of Dichlorobis(DL-valine)zinc(II) (DLVZC) was reported by Natarajan et al. [17]. Density functional theory (DFT) is very widely used to predict the structure of systems containing transition metals, vibrational wavenumbers and molecular hyperpolarizabilities [18–24].

In the present work, the structural geometry, vibrational spectra of synthesized DLVZC compound using both theoretical and experimental technique have been analyzed and reported. The natural bond orbital (NBO) analysis has been performed to explore interaction between (metal-ligands) inter- and intramolecular charge transfer and hydrogen bonding is explained. The global electrophilicity, chemical potential, hardness and softness have been calculated by Frontier molecular orbitals (FMOs) analysis. Hirshfeld surface maps and fingerprint plots to understand the various types of intermolecular interactions in a molecular crystal package are plotted. UV–Visible (UV–vis) spectral analysis has been carried out to identify the various electronic transitions. The

* Corresponding author.
E-mail address: hubertjoe@gmail.com (I. Hubert Joe).

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second-order hyperpolarizability of the synthesized DLVZC solution have been measured by open aperture (OA) and closed aperture (CA) methods using Z-scan technique.

2. Experimental method

2.1. Synthesis

The saturated aqueous solution of a mixture of DL-Valine and Zinc chloride in the stoichiometric ratio 1:1 was prepared with double distilled water. This prepared solution was stirred continuously for about 4 hours using a magnetic stirrer. Then the solution was filtered and kept at room temperature. After 45 days crystals were grown, which were purified by further recrystallization process and finally good quality crystals were obtained.

2.2. Characterization details

The powder X-ray diffraction (XRD) pattern of the Dichlorobis(DL-Valine)zinc(II) was received using a powder X-ray diffractometer (X'PERT – PRO Model, Nickel filtered CuKα radiations ($\lambda = 1.540$ Å)) at 30 mA, 40 kv. FT-IR spectrum of the sample was recorded in solid phase in the region from 4000 to 400 cm^{-1} using Perkin Elmer spectrophotometer at a resolution of 1 cm^{-1}. FT-Raman spectrum was recorded in the region from 3500 to 50 cm^{-1} using Bruker RFS 27 with standalone model with excitation wavelength of 1064 nm, the spectral resolution of 2 cm^{-1}. The UV–Visible absorption spectrum of the grown crystal was recorded in double distilled water solution using Varian Cary 100 B10 UV–vis spectrophotometer in the range of 200–800 nm. Third-order NLO properties of grown single crystal were investigated by OA and CA Z-scan technique with 5 ns Nd:YAG (neodymium-doped yttrium aluminium garnet) laser pulses at 532 nm and a repetition rate of 10 Hz.

3. Computational details

Quantum chemical computations were performed using the Gaussian 09 [25] program and visualize the results using GaussView 3.0 program [26]. The DLVZC molecular geometry and vibrational wavenumbers were computed by the DFT/Becke-3-Lee-Yang-Parr (B3LYP) [27] with 6–311++G(d,p) and LANL2DZ (Los Alamos National Laboratory 2 double ζ) level of basis sets. Furthermore, the vibrational modes were identified by potential energy distribution (PED) by VEDA4 program [28]. The calculated harmonic wavenumbers were scaled by a uniform scaling factor of 0.9673 (6-311++G(d,p)) and 0.961 (LANL2DZ) basis sets, neglecting vibrational anharmonicity. The calculated Raman activities were converted to relative Raman intensities using the theory of Raman scattering [29]. Hirshfeld surface map and fingerprint plots were generated using the program of CrystalExplorer 3.1 [30]. Electronic excitations and oscillator strengths were calculated using the time-dependent density functional theory (TD-DFT) method [31] at B3LYP/6-311++G(d,p) level of basis set. The solvent effects were calculated using TD-DFT in combination with the polarizable continuum model (PCM) developed by Tomasi and co-workers [32,33].

4. Results and discussion

4.1. Structural geometry

The X-ray data were collected using the X'Pert-Pro diffractometer. The powder X-ray diffraction data indicates that the DLVZC single crystal crystallizes in monoclinic system and space group *C*2/*c*. The lattice parameters are $a = 20.5104$ Å, $b = 6.2143$ Å, $c = 13.4125$ Å, cell angles $\alpha = \gamma = 90°$, $\beta = 102.3465°$ and Volume (V) = 1669.99 $Å^3$. The powder XRD pattern of DLVZC is shown in Fig. 1. When they are compared, the powder XRD data is in well matched with the reported value [17]. The observed diffraction pattern indexed and Miller indices were estimated by Indexing software package.

The global minimum energy of molecular structure obtained by 6–311++G(d,p) was −3504.98 hartrees, whereas LANL2DZ was −900.34 hartrees, respectively. For correlation between theoretical and experimental data, we considered only B3LYP/6-311++G(d,p) (−3504.98 hartrees) method, because it provides better result. The optimized molecular structure of the compound with atom numbering scheme is shown in Fig. 2. The crystallographic data and the optimized geometrical parameters are listed in Table 1. In the optimized structure, Zinc ion has a distorted

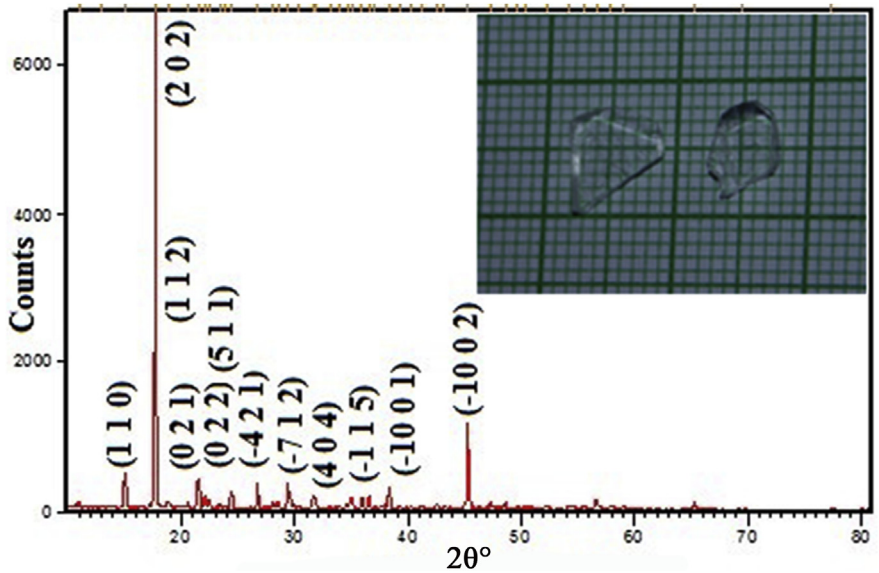

Fig. 1. Powder X-ray diffraction (Photographs of the grown crystals is shown in the inset figure) of DLVZC crystal.

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