

X-ray and infrared spectrum on metal complexes with indolecarboxylic acids

Part V. Catena-poly[$\{\text{aqua}(\eta^2\text{-indole-3-propionato-}O,O')\text{zinc}\}$ $-\eta^2\text{-}\mu\text{-indole-3-propionato-}O,O'\text{-}O\}$]

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Abstract

The catena-poly[$\{\text{aqua}(\eta^2\text{-indole-3-propionato-}O,O')\text{zinc}\}-\eta^2\text{-}\mu\text{-indole-3-propionato-}O,O'\text{-}O\}$, $[\text{Zn}(\text{I3PA})_2(\text{H}_2\text{O})]_n$, was prepared and characterized by infrared spectroscopy and X-ray structure determination. The crystals are monoclinic, space group Pc , with $a = 21.380(2)$, $b = 5.9076(7)$, $c = 8.1215(9)$ Å, $V = 1020.2(2)$ Å³ and $Z = 2$. The central zinc atom shows the coordination distorted from ideal octahedral. Each zinc centre is coordinated by two oxygen atoms of the bidentate chelating indole-3-propionato (I3PA), two oxygen atoms tridentate chelating-bridging I3PA, water molecule and one oxygen atom tridentate chelating-bridging I3PA from an adjacent $[\text{Zn}(\text{I3PA})_2(\text{H}_2\text{O})]$ unit. The infrared spectrum of $[\text{Zn}(\text{I3PA})_2(\text{H}_2\text{O})]_n$ in the solid state is supported by X-ray analysis. The theoretical wavenumbers and infrared intensities have been calculated by the density functional methods (B3LYP and mPW1PW) with the 6-311++G(d,p)/LanL2DZ basis sets. The theoretical wavenumbers, infrared intensities show a good agreement with experimental data. Detailed band assignment has been made on the basis of the calculated potential energy distribution (PED).

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1. Introduction

Indole-3-propionic acid, a deamination product of tryptophan is formed by symbiotic bacteria in the gastrointestinal tract of mammals and birds [1]. Indole-3-propionic acid may hold particular promise as a therapeutic agent in human brain diseases [2]. It was found that anti-inflammatory and anti-bacterial activity of metal complexes was higher than in the parent carboxylic acids [3]. Zinc and its compounds have anti-bacterial, anti-viral activity and the wound-healing effect of zinc-containing ointments has been known for several centuries [3]. Moreover, important application of polymerization reactions is in the quest for dental filling materials as a substitute for amalgams [4]. The carboxylate group display a variety of binding geometries, such as monodentate, chelating,

bidentate bridging and monodentate bridging so in coordination chemistry as well as in the active sites of metalloenzymes [5–9]. It should be noted that the crystal structures of indole-3-propionic acid have been reported [10,11], but no single crystal X-ray diffraction analysis has been performed for its metal complexes, as yet.

In our previous papers, in Parts I and II, the crystal and molecular structure of indole-2-carboxylic acid and its derivative 5-methoxyindole-2-carboxylic acid have been reported [12,13]. In Parts III and IV, we studied diamminetetraakis(μ -indole-3-carboxylato- O,O')dicopper(II) (Cu-I3CA) and catena-poly[$\{\text{aqua}(\eta^2\text{-indole-3-carboxylato-}O,O')\text{zinc}\}-\mu\text{-indole-3-carboxylato-}O,O'\}$ ($[\text{Zn}(\text{I3CA})_2(\text{H}_2\text{O})]_n$) complexes by single crystal X-ray diffraction analysis, EPR and infrared and Raman spectroscopic methods and the density functional calculations [14,15]. In the present paper, $[\text{Zn}(\text{I3PA})_2(\text{H}_2\text{O})]_n$ is examined using single crystal X-ray diffraction analysis and the infrared spectrum. We attempted to present a detailed interpretation of the observed infrared spectrum

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employing for this theoretical calculations the B3LYP and mPW1PW methods. The characters of computed normal vibrations are shown in terms of potential energy distribution.

2. Experimental

2.1. Preparation of crystals of $[Zn(I3PA)_2(H_2O)]_n$

Crystals of $[Zn(I3PA)_2(H_2O)]_n$ were prepared as follows: to a suspension of 0.14 g of $ZnCl_2 \cdot 2H_2O$ and 2 cm^3 1 M NaOH, the solution of 0.19 g of indole-3-propionic acid (Lancaster) in ethanol (50 cm^3) was added. The mixture was heated to 318 K for about 1 h. The obtained solution was filtered and left for crystallization. After 1 week, the translucent crystals of $[Zn(I3PA)_2(H_2O)]_n$ were formed.

Anal. found: C, 57.86%; H, 4.70%; N, 6.18%; Zn, 14.42%. Calc. for $C_{22}H_{22}ZnN_2O_5$: C, 57.47%; H, 4.82%; N, 6.09%; Zn, 14.22%.

2.2. X-ray analysis

The X-ray diffraction data were collected at 290(2) K, using a XCALIBURTM 3 CCD diffractometer with graphite-monochromated Mo K α radiation ($\lambda = 0.71073\text{ \AA}$). The structure was solved by direct methods using SHELXS-97 program [16] and refined by full-matrix least-squares on F^2 with SHELXL-97 [16]. The hydrogen atoms bonded to C and N atoms were introduced at calculated positions as riding atoms, with C–H and N–H distances of 0.93 and 0.86 \AA , respectively, while the O-bound H atoms were located from difference maps. The O–H distances were restrained with a DFIX command in SHELXL-97 [16]. For all H atoms, $U_{iso}(H)$ values were constrained to be $1.2 U_{eq}(C, N)$ or $1.5 U_{eq}(O)$.

The crystal data together with the refinement details are given in Table 1. Atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre and allocated under the deposition number CCDC 299568.

2.3. Spectroscopic measurements

The infrared spectrum of solid $[Zn(I3PA)_2(H_2O)]_n$ in the region $4000\text{--}400\text{ cm}^{-1}$ was measured at 2 cm^{-1} resolution on a Nicolet–Nexus spectrometer using the KBr pellets. The far infrared spectrum in the frequency range $700\text{--}50\text{ cm}^{-1}$ was measured at 2 cm^{-1} resolution on a Perkin-Elmer 2000 spectrometer. Sample was prepared as Nujol mulls placed between polyethylene windows.

2.4. Theoretical methods

The theoretical studies have been performed using the density functional three-parameter hybrid, B3LYP [18,19] and one-parameter hybrid, mPW1PW, introduced by Adamo and Barone [20] methods with the LanL2DZ [21,22] for zinc and 6-311++G(d,p) [23,24] basis sets for the remaining atoms. In the case of polymeric complexes, the extent of computational model is important for good reproduction of infrared spectrum

Table 1
Crystal data and structure refinement for $[Zn(I3PA)_2(H_2O)]_n$

Empirical formula	$C_{22}H_{22}ZnN_2O_5$
Formula weight	459.81
Temperature (K)	290(2)
Crystal system	Monoclinic
Space group	Pc
Unit cell dimensions (\AA , $^\circ$)	$a = 21.380(2)$ $b = 5.9076(7)$ $c = 8.1215(9)$ $\beta = 95.985(9)$
Volume (\AA^3)	1020.2(2)
Z (molecule/cell)	2
Density calculated (Mg m^{-3})	1.497
Crystal size (mm)	$0.16 \times 0.15 \times 0.03$
Absorption coefficient (mm^{-1})	1.241
Absorption correction	Analytical [17]
$F(0\ 0\ 0)$	476
Theta range for data collection ($^\circ$)	$0.96\text{--}25.68$
Reflections collected	2469
Independent reflections	2469
Data/restraints/parameters	2387/4/278
Goodness-of-fit on F^2	1.072
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0455$, $wR_2 = 0.0697$
R indices (all data)	$R_1 = 0.0484$, $wR_2 = 0.0706$
$\Delta\rho_{max}$ and $\Delta\rho_{min}$ ($e\text{\AA}^{-3}$)	0.361, -0.386
Δ/σ_{max}	0.000
Flack parameter	0.0(4)

of the polymeric complex. For this purpose, two models M1 and M2 were chosen, by selecting the respective parts of the complex polymer (Fig. 1). The theoretical model M1 was limited to coordinating aqua and bidentate chelating I3PA representing the ligands bonded to one zinc(II) via two oxygen atoms. The theoretical model M2 was limited to coordinating aqua and tridentate chelating-bridging I3PA representing the ligands bonded to two zinc(II) ions via two oxygen atoms. Prior to normal mode computations, the optimization of molecular geometry was carried out starting from structural parameters determined by the X-ray method. Basing on the optimized structures for M1 and M2 models, the normal vibration wavenumbers and IR intensities were calculated. The normal coordinate analysis for M1 and M2 models have been carried out, including the calculation of the potential energy distribution (PED) for each normal mode, according to the procedures described in ref. [25] (BALGA program). The non-redundant set of internal coordinates has been derived, as recommended by Fogarasi and Pulay [26–28].

The computations were carried out with the Gaussian 03 programs [29] on multiprocessor SGI Origin 2400 super-computer.

3. Results and discussion

3.1. Description of the structure of $[Zn(I3PA)_2(H_2O)]_n$

The overall view and labeling of the atoms in the $[Zn(I3PA)_2(H_2O)]_n$ are displayed in Fig. 1. The carboxylate oxygen atoms are directly involved in coordination to a zinc

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