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Concomitant polymorphism of an octahedral, homoleptic zinc(II) bis complex of an N,N,O donor hydrazone

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ABSTRACT

Using the 1:1 condensate of benzil and 2-hydrazinopyridine as the ligand HL (H: a dissociable proton), a new zinc(II) complex ZnL_2 is synthesized. It is obtained as a mixture of three types of deep red crystals – diamond shaped (**1a**), rectangular (**1b**) and pointed tetragonal (**1c**) which can be separated manually. Their different crystal structures have been determined. **1a** crystallizes in the space group $P2_1/c$, **1b** in Pbca and **1c** in P-1. The asymmetric unit of **1c** contains two independent molecules labeled A and B. Thus ZnL_2 can assume at least four different molecular conformations in the solid state, namely **1a**, **1b**, **1c**-A and **1c**-B. But in the DFT calculations at the B3LYP/6-311++G (2d,p) and BP86/LanL2DZ levels **1a**, **1b**, **1c**-A and **1c**-B converge to a single structure in the gas phase. The DFT structure is found to possess a C_2 axis though no symmetry constraint was imposed in the calculations. Interestingly **1a**, **1b**, **1c**-A and **1c**-B yield the same NMR spectra in solution revealing a C_2 axis. So it is concluded that the gas phase DFT structure is realized experimentally only in solution. Further, our DFT calculations show that the four species are distributed along a “potential energy curve” of ZnL_2. Anyway, our ZnL_2 presents a case of concomitant polymorphism.

1. Introduction

Crystallization and subsequent X-ray structure determination are very important in understanding the physico-chemical behaviour of a molecule. Some molecules have the property of crystallizing in more than one distinct structure, which is called polymorphism [1–7]. Such properties are of much current interest because of medicinal values which at times depend on the form [6,8,9]. Crystallization of polymorphs is still not well understood. In some cases more than one polymorph can crystallize simultaneously which is termed as concomitant polymorphism [10]. Consequently, reproducibility of a polymorph sometimes becomes a problem. The first important principle in this regard is possibly Ostwald step rule formulated in 1897 – if a molecule can crystallize in more than one form then in a single experiment the least stable one will crystallize first [4,11–13]. A principle of interest mainly to the inorganic chemists is that formulated by Basolo in 1968 [14], which states that “solid salts separate from … solution easiest for combinations of either small cation-small anion or large cation-large anion, preferably with systems having the same but opposite charges on the counterions”. Earlier, we have recognized an unproliferating effect of an anion exerted on the countercations – “the tendency of polymerization in the cation decreases as the size of the counteranion increases” [15]. Whatever the reason for crystallization of a particular form, the crystal structure is always characterized by a corresponding energy minimum on its potential energy surface (PES). In this context it is mentioned that recently we have delineated an experimental PES for the pentachlorocuprate(II) anion [16]. A common experience in computational chemistry is that though a structure may display an energy minimum, it may not be possible to realise the structure experimentally. The most noted example is unsubstituted cyclobutadiene. Though it shows a global energy minima [17], so far it has eluded the synthetic chemists [18]. Herein we report concomitant polymorphism of a zinc(II) complex. The various forms characterized structurally are somewhat different from the gas phase structure established by DFT.

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2. Experimental

2.1. Materials and physical measurements

The ligand benzilmono-(2-pyridyl)hydrazone (HL) was synthesized by the procedure reported by Tomlinson and co-workers [19]. Elemental analyses were performed by a Perkin-Elmer 2400II CHNS analyser. FTIR spectra (KBr) were recorded on a Shimadzu FTIR-8400S spectrometer and UV-Vis (CH_3OH) spectra on a Perkin Elmer Lambda 950 spectrophotometer. 500 MHz NMR spectra ($CDCl_3$) were recorded on a Bruker Avance III 500 spectrometer and ESI mass spectra (CH_3CN) on a Waters Qtof Micro YA263 spectrometer.

2.2. Synthesis of bis(benzilmono-2-pyridylhydrazonato)zinc(II) (**1a**, **1b** and **1c**)

$Zn(ClO_4)_2.6H_2O$ (0.037 g, 0.1 mmol) was dissolved in 10 mL methanol and added dropwise to a 10 mL methanol solution of HL (0.06 g, 0.2 mmol) and stirred at room temperature. Triethylamine (0.02 g, 0.2 mmol) was added to the reaction mixture and stirred for 4 h. A red microcrystalline precipitate appeared which was filtered and washed with *ca*. 5 mL cold methanol. The compound was dried in air. Yield: 0.04 g, (67%). Recrystallisation from hot methanol produced red single crystals. Three types of crystals – diamond shaped (**1a**), rectangular (**1b**) and pointed tetragonal (**1c**) were obtained. They were separated manually. All of them analysed as ZnL_2. Anal. Calc. (found, %) for $C_{38}H_{28}N_6O_2Zn$: C 68.52 (68.34), H 4.24 (3.99), N 12.62 (12.61). **1a**, **1b** and **1c** displayed same NMR, FTIR and ESI-MS spectra. ^{1}H NMR: δ, ppm: 7.71 (d, 2H), 7.57–7.62 (m, 2H), 7.36–7.44 (m, 12H), 7.26–7.32 (m, 6H), 7.16 (t, 4H), 6.78 (t, 2H). FTIR (cm^{-1}): 3056 (w), 1600 (w), 1442 (w), 1319 (m), 1213 (s), 1778 (m), 1141 (m), 1089 (m), 1000 (m), 931 (m), 744 (w), 698 (w), 661 (w). ESI-MS (positive ion mode): $m/z = 302.35$ (100%, $[LH + H]^+$). UV-VIS λ_{max}/nm ($\varepsilon_{max}/dm^3\ mol^{-1}\ cm^{-1}$): 264 (22 400), 334 (30 500), 485 (32 400).

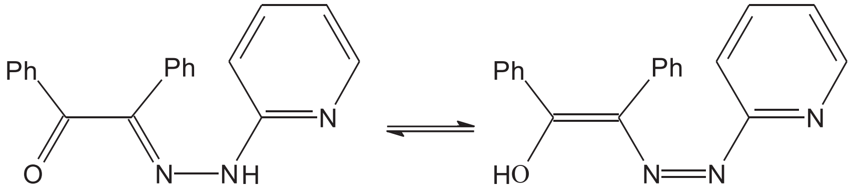
2.3. X-ray crystallography

Data for **1a** were collected with MoKα using the Oxford Diffraction Xcalibur CCD System and for **1b** and **1c** using a Bruker APEX II CCD diffractometer. Crystals of **1a** were positioned at 50 mm from the CCD and 321 frames were measured with counting times of 10 s. Data analysis was carried out with the CrysAlis program [20]. Data analyses for **1b** and **1c** were performed by software built in APEX II. The structures were solved using direct methods with the Shelxs97 program [21]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. In **1b**, one of the phenyl rings was disordered over two orientations with occupation factors of x and 1-x, x refining to 0.61(2). In **1c** there are two molecules in the asymmetric unit called A and B. Absorption corrections for **1a** were carried out using the ABSPACK program [22] and for **1b** and **1c** by SADABS available in APEX II. The structures were refined on F^2 using Shelxl97 [21].

3. Results and discussion

The zinc(II) species studied here is a neutral bis complex of the ligand HL (H: a dissociable proton), which is a 1:1 condensate of benzil and 2-hydrazinopyridine. The ligand is known since 1964 [19]. It can exist in two forms – keto and enol (Scheme 1). In solid state, it exists in the keto form [23]. In a metal complex, deprotonation may occur [12,24] and the ligand adopts the enolate form. When HL is not deprotonated upon binding a metal ion, N–H stretch is observed in the IR spectrum [24].

The Zn(II) complexes are prepared by reacting HL with $Zn(ClO_4)_2.6H_2O$ in methanol in 2:1 M proportions at room temperature in the presence of a base like triethylamine as red compounds. Recrystallisation of the product from hot methanol yields three types of deep red crystals – diamond shaped (**1a**), rectangular



Scheme 1. Tautomerisation in HL.

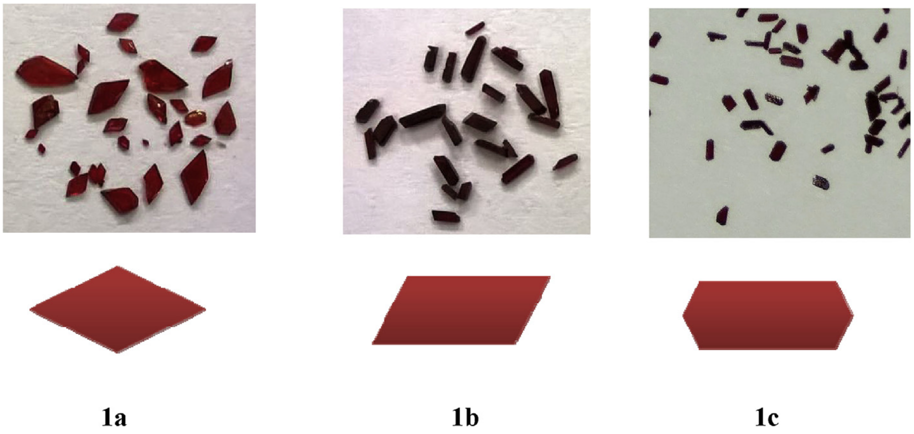


Fig. 1. Morphologies of the various types of single crystals of ZnL_2: diamond shaped, **1a**; rectangular, **1b**; pointed tetragonal, **1c**.