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Isomerism and nuclearity control in bis(lawsonato)zinc(II) complexes

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ABSTRACT

This work aims to provide new insights concerning isomerism and nuclearity control in lawsone complexation reactions, as well as exploit physical and chemical properties related to different structural features. Three new bis(lawsonato)zinc(II) complexes, *cis,cis,cis*-$[ZnL_2(H_2O)_2]\cdot 2H_2O$ (**1**), *trans,trans,trans*-$[ZnL_2(H_2O)_2]$ (**2**) and $[Zn_2L_4(py)_2]\cdot 2H_2O$ (**3**), were synthesized and characterized by X-ray crystallography, thermogravimetric analysis, ^1H NMR, IR and UV–Vis spectroscopies and cyclic voltammetry. It has been demonstrated that, for the reaction between zinc(II) and lawsone, the coordination geometry and nuclearity of the product can be directed by modifying the addition sequence of the reactants and the nature of the base (pyridine versus triethylamine). Complex **1** has a zinc(II) ion coordinated by two lawsonate anions and two water molecules in a *cis* configuration, in a distorted octahedral environment. On the other hand, the structure of **2** differs from **1** mainly by the *trans* conformation of the ligands. Complex **3** has a dinuclear structure with an inversion center lying between the two metal centers, where each one of the two zinc atoms is coordinated by two lawsonate anions in a *cis* configuration and by one pyridine molecule. When dissolved in dmso, however, all data indicate that complexes **1**–**3** are converted to one single species, $[ZnL_2(dmso)_2]$.

1. Introduction

The pharmacological properties of naturally occurring 1,2- and 1,4-naphthoquinone nuclei and their derivatives have been a subject of increasing interest [1]. Such molecules present a large variety of activities including bactericide [2–4], fungicide [5], anti-viral [6,7], antitumoral [8–10], trypanocidal [11,12] and antimalarial [13,14] properties, which are usually related to their capability of being reduced by one electron to form a semiquinone radical [15]. In biological systems, reduction mediated by reductases generates reactive oxygen species (ROS) that cause DNA damage, oxidative stress and apoptosis among other harmful effects [16]. Modulation of the reactivity by changing the chemical environment of the naphthoquinones (NQs) has been attempted, in order to improve their pharmacological activities and reduce side effects [17–19]. It is known that the coordination of NQs to metal ions is a way of modifying their redox potential and stabilizing the semiquinone intermediate [20]. Increase on the cytotoxicity of 2-hydroxy-1,4-NQ (lawsone) derivatives upon coordination has being reported in studies of copper complexes with buparvaquone [21] and azo derivatives of lawsone [22–24]. Surprisingly, the coordination chemistry of lawsone (Fig. 1) has not been fairly exploited. Special attention was given to $[Fe(lawsonato)_2(H_2O)_2]$, since this complex has been firstly described as a mimetic model for the photosynthetic bacterial reaction center [25–27], and later submitted to biological tests [28]. Recently, Rane and co-workers have evaluated spectroscopic and magnetic properties of $[Cu(lawsonato)_2(H_2O)_2]$ [29]. Other spectroscopic and electrochemical studies on compounds of formula $[M(lawsonato)_2(py)_2]$, M = Co(II), Ni(II), Zn(II) [20] have been reported by Frontana and co-workers. In order to improve the knowledge about the coordination chemistry of lawsone and its derivatives, as well as the effects of coordination on the biological activities, we report here an investigation regarding synthesis and structural, electrochemical and spectroscopic characterization of the complexes *cis,cis,cis*-$[ZnL_2(H_2O)_2]\cdot 2H_2O$ (**1**), *trans,trans,trans*-$[ZnL_2(H_2O)_2]$ (**2**) and $[Zn_2L_4(py)_2]\cdot 2H_2O$ (**3**) (L = lawsonate). To the best of our knowledge, the geometric isomerism found for $[ZnL_2(H_2O)_2]$ is an unprecedented occurrence concerning 2-hydroxy-1,4-NQ complexes. Therefore, this work aims to provide new insights concerning isomerism and nuclearity control in lawsonate complexation reactions, as well as to exploit physical and chemical properties related to different structural features.

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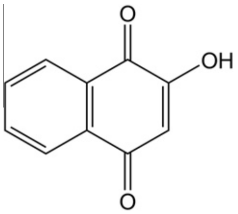

Fig. 1. 2-Hydroxy-1,4-naphthoquinone (lawsone).

2. Experimental

2.1. Materials and instrument details

All chemicals were used as received without further purification. Infrared spectra were recorded on a Bomen FTLA 2000 FTIR spectrophotometer using KBr pellets (resolution: 4 cm^{-1}). ^1H NMR spectra were obtained on a Varian Unity-Plus 500 MHz spectrometer, in dmso-d_6. Thermogravimetric analysis (TGA) were carried out in a 25–500 °C temperature range with a Shimadzu TA-60WS Thermal System, under nitrogen flow (50 mL min^{-1}) and a heating rate of 10 °C min^{-1}. UV–Vis spectra were collected on a Varian Cary 50 Spectrophotometer from dmso solutions. The spectrum of free lawsonate was measured from a solution of lawsone in dmso upon addition of NaOH 1:5. Cyclic voltammetry experiments were performed on a BAS Epsilon Potenciostat-Galvanostat at room temperature, under argon atmosphere (99.999% pure), using 1×10^{-3} mol L^{-1} solutions of the complexes in anhydrous dmso, containing 0.1 mol L^{-1} of $TBAClO_4$ (supporting electrolyte). A standard three-component system was used: a glassy carbon working electrode, a platinum wire auxiliary electrode, and an Ag/AgCl reference electrode for organic media. Ferrocene was used as an internal reference [30]. Microanalysis were performed using a Perkin-Elmer CHN 2400 micro analyzer at Universidade de São Paulo (USP-SP), Brazil.

2.2. X-ray crystallography

A Bruker Kappa CCD diffractometer (Mo Kα radiation) was used to collect data on suitable single crystals. The data collection was made with the COLLECT software [31]. The cell parameters and its symmetry were determined utilizing the software Ndirax [32]. The structures were solved by direct methods using SHELXS-97 and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique [33]. The hydrogen atoms, with exception of those of water molecules and hydroxyl groups, were generated geometrically. All calculations were performed on a personal computer with the SHELXL-97 crystallographic software package [33]. Crystal data are given in Table 1. Powder diffraction measurements were made on a Bruker D8 Advanced diffractometer with Cu Kα graphite-monochromatized radiation between 5° and 40° with a step of 0.04° collecting 2 s each step.

2.3. Syntheses

2.3.1. *Cis,cis,cis-diaquabis(lawsonato)zinc(II) dihydrated, cis,cis,cis-*$[ZnL_2(H_2O)_2]\cdot 2H_2O$ (**1**)

Lawsone (0.35 g, 2.0 mmol) was dissolved in 15 mL of methanol and zinc acetate dihydrated (0.22 g, 1.0 mmol) previously dissolved in 10 mL of water was then added slowly, followed by 0.28 mL (2.0 mmol) of triethylamine. The reaction mixture was left stirring at room temperature for 2 h. A red powder precipitate was then removed by filtration, washed with cold methanol and dried under vacuum (yield = 77%). *Anal.* calc. for $C_{20}H_{18}O_{10}Zn$: C, 49.66; H, 3.75%. Found: C, 50.99; H, 3.63%. UV–Vis [dmso, λ/nm (log ε)]: 476 (*3.76*). Slow evaporation of the mother liquor produced a crystalline precipitate, from where X-ray suitable single crystals were separated. IR (4000–600 cm^{-1}, KBr): 3200 br (O–H); 1650 m, 1611 m (C=O); 1589 s, 1549 m (C=C); 1278 s (C–O); 736 m (C–H).

2.3.2. *Trans,trans,trans-diaquabis(lawsonato)zinc(II), trans,trans,trans-*$[ZnL_2(H_2O)_2]$ (**2**)

Zinc acetate dihydrated (0.22 g, 1.0 mmol) was dissolved in 10 mL of distillate water and 15 mL of a methanol solution of lawsone (0.35 g, 2.0 mmol) and triethylamine (0.28 mL, 2.0 mmol) was then slowly added. The reaction mixture was left stirring at room temperature for 2 h. A red powder precipitate was then separated by filtration, washed with cold methanol and dried under vacuum (yield = 76%). *Anal.* calc. for $C_{20}H_{14}O_8Zn$: C, 53.65; H, 3.15%. Found: C, 53.89; H, 2.90%. UV–Vis [dmso, λ/nm (log ε)]: 476 (*3.76*). X-ray suitable single crystals were separated after slow evaporation of the mother liquor. IR (4000–600 cm^{-1}, KBr): 3340 br (O–H); 1642 m, 1610 m (C=O); 1585 s, 1558 s (C=C); 1278 s, 1252 m (C–O); 732 w (C–H).

2.3.3. *Bis-[bis-(lawsonato)pyridinezinc(II)] dihydrated,* $[Zn_2L_4(py)_2]\cdot 2H_2O$ (**3**)

Zinc acetate dihydrated (0.44 g, 2.0 mmol) was dissolved in 10 mL of methanol and 20 mL of a methanol solution of lawsone (0.70 g, 4.0 mmol) and pyridine (1.0 mL, 7.2 mmol) was then added. The resulting solution was left stirring overnight. A red powder precipitate was then separated by filtration, washed with cold methanol and dried under vacuum (yield = 68%). *Anal.* calc. for $C_{50}H_{34}O_{14}N_2Zn_2$: C, 59.01; H, 3.37; N, 2.75%. Found: C, 59.10; H, 3.29; N, 2.87%. λ/nm (log ε)]: 470 (*4.05*). X-ray suitable single crystals were separated after slow evaporation of the mother liquor. IR (4000–600 cm^{-1}, KBr): 3539 w, 3451 w (O–H); 1643 m (C=O); 1591 s, 1557 s (C=C); 1271 s, 1245 m (C–O); 737 w (C–H).

3. Results and discussion

3.1. Syntheses

The reaction of zinc(II) acetate with lawsone produces two different complexes, *cis,cis,cis*-$[ZnL_2(H_2O)_2]\cdot 2H_2O$ (**1**) and *trans, trans,trans*-$[ZnL_2(H_2O)_2]$ (**2**), depending on the addition sequence of the reactants. When a zinc(II) solution is slowly added onto a solution of lawsone, followed by the addition of triethylamine, the *cis* complex (**1**) is obtained. The *trans* complex (**2**) is formed by the dropwise addition of a solution containing lawsone and triethylamine onto a zinc(II) solution. Pure *cis* and *trans* isomers were isolated as red solids that precipitate in up to two hours after starting the reaction. When solutions of **1** and **2** are left undisturbed for few days, a mixture of both complexes co-crystalized as plate and needle shaped crystals (Supp. Info., Fig. S1). The plates were identified as the *cis*-isomer (**1**) and the needles as the *trans*-isomer (**2**) by single crystal X-ray crystallography. The dinuclear complex $[Zn_2L_4(py)_2]\cdot 2H_2O$ (**3**) is isolated as a red powder precipitate, when a methanol solution containing lawsone and excess of pyridine is added to a methanol solution of zinc(II). Interestingly, Frontana and co-workers [20] described a mononuclear $[Zn(law)_2(py)_2]$ complex, with two pyridine ligands coordinated to the metal in a *cis* configuration, from a reaction in which excess of pyridine is added to a methanol solution containing the metal ion and lawsone. X-ray suitable single crystals of **3** were obtained after leaving the mother liquor rest undisturbed for a few days. The microcrystalline powders obtained from the synthesis of complexes **1**–**3** were also analyzed by X-ray powder