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Synthesis, crystal structure and spectrothermal characterization of zinc(II) salicylato complex with 2,2′-azobispyridine, $[Zn(Hsal)_2(H_2O)(abpy)]\cdot H_2O$

Figen Arslan*

Department of Chemistry, Ondokuz Mayıs University, TR-55139, Kurupelit, Samsun, Turkey

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Abstract

The novel aqua(azobispyridine)bis(salicylato)zinc(II) monohydrate complex (**1**) was synthesized and characterized by means of elemental analysis, IR and UV-vis spectroscopy, thermal analysis and X-ray diffraction techniques. The crystal structure analysis indicates that the mononuclear **1** shows an *s-cis*/*E*/*s-cis* configured azobispyridine ligand, with the distortion from square pyramidal toward trigonal bipyramidal Zn(II) ion coordinated to one pyridyl and one azo N atom together with two carboxylate oxygen atoms and one aqua ligand. The crystal packing involves both hydrogen-bonding and π−π interactions. The title complex undergoes a thermochromic phase transition at ca. 189 °C, changing from **1** (brown complex) to **2** (purple complex) and the thermal decomposition of **1** proceeds in four stages.

Keywords: Azobispyridine; Thermochromism; Salicylato complex; Zinc complex; Spectrothermal analysis

1. Introduction

Salicylic acid and metal salicylates have been used for many years as anti-inflammatory, antipyretic and analgesic drugs in medicine [1−3]. In aqueous solutions, the acid affords hydrogensalicylate ($Hsal^-$) and salicylate (sal^{2-}) ions. The $Hsal^-$ anion can bind to metals as unidentate carboxylate, bidentate chelating (employing one carboxylate oxygen and hydroxyl oxygen atoms) or bidentate bridging carboxylate ligand. The studies of the material chemistry of the azoaromatic compounds have attracted increasing attention because of their unique combination of geometrical and electronic structures [4−7]. The 2,2′-azobispyridine (abpy), derived from the 2,2′-bipyridine through the insertion of the azo (diazene) group between the two pyridyl moieties is known to form an unusual complex [8]. The abpy ligand has several different coordination modes involving five-membered chelate ring formation (N═N−C−N−M), as shown in Scheme 1. When one 2-pyridyl ring remains uncoordinated, because of the repulsion effects between azo N-atom lone pairs and *ortho*-CH or pyridyl N-atom lone pairs, a singly chelating complex can form, as in **IIa** or **IIb**. The abpy ligand rings can also involve in π−π and π−ring interactions, forming extended networks of supramolecular architectures [9,10]. These types of interactions have attracted particular attention especially in fields such as developing new functional materials, crystal engineering, molecular recognition and self-assembly of organometallic compounds [11,12]. The aim of this work was to prepare a new mixed-ligand salicylato complex of Zn(II) with 2,2′-azobispyridine and undertake its crystal structure and spectrothermal analysis.

2. Experimental

2.1. Synthesis of 1

Sodium salicylate (1.11 g, 6.96 mmol) was dissolved in water (50 ml) and added to the 50 ml of hot water solution of

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* Fax: +90 362 4576081.
E-mail address: farslan@omu.edu.tr

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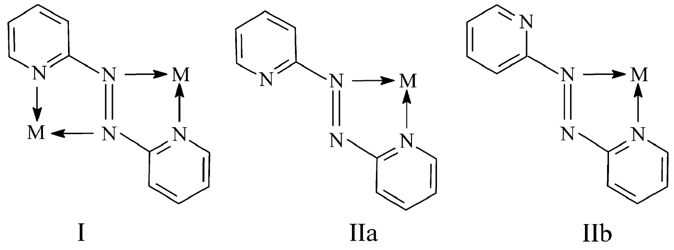

Scheme 1.

$ZnSO_4 \cdot 7H_2O$ (1.0 g, 3.48 mmol). The mixture was stirred at 323 K for 3 h and then cooled to room temperature. The crystals formed were filtered off and washed with water and acetone, and dried in a vacuum. Abpy was prepared following the method of Rivarola et al. [13]. A solution of abpy (0.11 g, 0.61 mmol) in acetonitrile (20 ml), was added dropwise with stirring to a solution of $[Zn(Hsal)_2(H_2O)_4]$ (0.25 g, 0.61 mmol) in acetonitrile (50 ml). The mixture was refluxed for 1 h and then cooled to room temperature. After a couple of weeks, well-formed brown crystals were selected for X-ray studies. Yield for **1**: 58%. Elemental analysis, found (calculated for $C_{24}H_{22}ZnN_4O_8$): C, 51.75 (51.49); H, 3.36 (3.96); N, 9.83 (10.00).

2.2. Physical measurements

All chemicals used were analytical reagent products. Elemental analyses were performed by standard methods at TÜBİTAK (The Turkish Scientific Research Centre). The UV–vis spectrum of **1** was obtained with a Unicam UV2 spectrometer in the 900–190 nm range. The IR spectrum was recorded on a Jasco 430 FT/IR spectrophotometer using KBr pellets and operating at 4000–200 cm^{-1}. TG8110 thermal analyzer was used to record TG, DTA and DTG curves in a static air atmosphere at a heating rate of 10 $K\,min^{-1}$ in the temperature range 20–1000 °C using platinum crucibles. Highly sintered α-Al_2O_3 was used as a reference and the DTG sensitivity was 0.05 $mg\,s^{-1}$.

2.3. Crystal structure analysis

Data collection was performed on a STOE IPDSII image plate detector using Mo Kα radiation ($\lambda = 0.71019$ Å). Details of crystal structure are given in Table 1. Data collection: Stoe X-AREA [14]. Cell refinement: Stoe X-AREA [14]. Data reduction: Stoe X-RED [14]. The structure was solved by direct methods using SHELXS-97 [15] and anisotropic displacement parameters were applied to non-hydrogen atoms in a full-matrix least-squares refinement based on F^2 using SHELXL-97 [15]. Molecular drawing was obtained using ORTEP-III [16].

Table 1
Crystallographic data for **1**

Formula	$C_{24}H_{19}N_4O_7Zn \cdot H_2O$
Molecular weight	558.84
Temperature	293 (2) K
Wavelength	0.71069 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	$a = 9.0600$ (8) $b = 9.8260$ (7) $c = 15.2270$ (12) $\alpha = 104.345$ (6) $\beta = 92.391$ (7) $\gamma = 109.771$ (6)
Volume	1224.11 (17) $Å^3$
Z	2
Calculated density	1.516 $mg\,m^{-3}$
μ	1.060 mm^{-1}
$F(000)$	727.8
Crystal size	0.3 × 0.2 × 0.1 mm
θ Range	2.29–27.97°
Index ranges	$-11 \leq h \leq 11$ $-12 \leq k \leq 12$ $-20 \leq l \leq 20$
Reflections collected	17,874
Independent reflections	5831
Reflections observed (>2σ)	4430
Absorption correction	Integration
Max. and min. transmission	0.7152–0.8564
Refinement method	Full-matrix least-squares on F^2
Data/restrains/parameters	5774/110/397
Goodness-of-fit on F^2	1.042
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0415$, $wR2 = 0.1012$
R indices (all data)	$R1 = 0.0588$, $wR2 = 0.1093$
Largest diff. peak and hole	0.329 and −0.670 $Å^{-3}$

In the refinement of **1**, H atoms of the aqua and lattice water molecules were located from a difference Fourier map, while the other H atoms were placed at calculated positions (C–H = 0.93 Å) and were allowed to ride on their parent atoms [$U_{iso}(H) = 1.2U_{eq}(C)$]. The disordered o-hydroxyphenyl group [site-occupancy factors of 0.602 (7) for A group and 0.397 (7) for B group] was refined anisotropically, with constraints and restraints imposed C–C and C–O distances, and the anisotropic displacement parameters of the C and O atoms. H atoms attached to O17A and O17B were not located.

3. Results and discussion

3.1. Description of the crystal structure

The asymmetric unit of the complex consists of one **1** unit. One of the o-hydroxyphenyl groups is disordered over two positions, with occupancies of 0.6 for A group and 0.4 for B group (Fig. 1). The Zn(II) ion is coordinated by two salicylate oxygen atoms [Zn1–O2 = 1.9682 (19) Å, Zn1–O5 = 2.007 (2) Å], two abpy nitrogen atoms [Zn1–N1 = 2.081 (2) Å; Zn1–N3 = 2.301 (2) Å], and an aqua ligand [Zn1–O1 = 2.044 (2) Å]. These bond distances are found to be similar to those of related Zn(II) complexes [17,18]. All N–Zn1–N, N–Zn1–O and O–Zn1–O bond angles deviate significantly from 90, 120, and 180° due most probably to the result of steric constraints arising from the shape of the ligands. The angle subtended at the Zn1 atom by the abpy ligand is 72.61 (7)°, which is in agreement with the value of our previously reported study for abpy-containing Cu(II) complex [10]. The