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Dyes and Pigments 75 (2007) 521–525
DYES and PIGMENTS
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Synthesis, crystal structure and spectrothermal characterization of zinc(II) salicylato complex with 2,2′-azobispyridine, $[Zn(Hsal)_2(H_2O)(abpy)]\cdot H_2O$

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Received 22 January 2006; received in revised form 19 April 2006; accepted 28 June 2006
Available online 8 September 2006

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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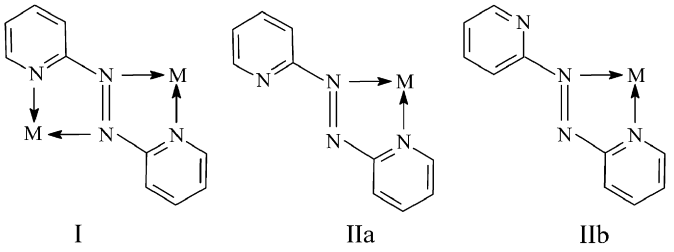
doi:10.1016/j.dyepig.2006.06.035



I IIa IIb

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].

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.

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	$-11 \le h \le 11$
	$-12 \le k \le 12$
	$-20 \le l \le 20$
Reflections collected	17,874
Independent reflections	5831
Reflections observed ($>2\sigma$)	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 $Å^{-3}$

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

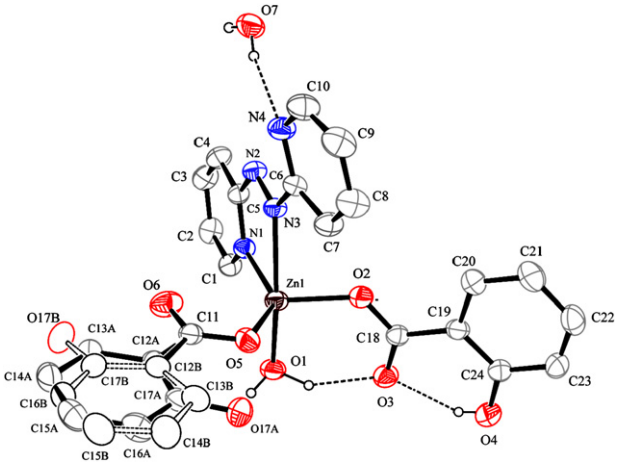


Fig. 1. The molecular structure of **1**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

almost linear O1–Zn1–N3 [165.80 (8)°] moiety has the appearance of the axis in a rough trigonal bipyramid, in which the equatorial positions are occupied by two salicylate oxygen atoms and pyridyl nitrogen atom, while the axial positions are occupied by one aqua ligand and one azo N atom. The degree of trigonality $\tau = 0.47$ [τ is defined by Addison et al. [19] for the regular square-pyramidal (SQP) structure, the trigonality parameter 0, and for the trigonal-bipyramidal (TBP) structure, it increases to 1] indicates a significant deformation of the observed SQP coordination of the Zn1 atom toward TBP coordination. The Zn atom deviates by 0.1531 (9)° from the basal plane toward the apical O1 atom.

Formation of the mono-chelate complex of abpy ligand makes structural alternatives **IIa** and **IIb** for the remaining uncoordinated pyridyl ring. Existing studies of its coordination modes demonstrate that X-ray analysis data available for [(abpy)$CuCl_2H_2O$]·H_2O [10], (abpy)$Mo(CO)_4$ [20], (abpy)$Re(CO)_3Cl$ [5], [(abpy)Ru]$(PF_6)_2$ [21] come close to situation **IIb** with the pyridyl-N directed toward the chelate metal atom. But in this paper, it can be seen that the abpy ligand adopts an *s-cis/E/s-cis* conformation, although it adopts in above references *s-cis/E/s-trans* conformation. This is apparantly due to the intermolecular hydrogen-bonding interaction between atom H11 of the crystal water molecule and the free pyridyl N atom (Table 2). In **1**, the salicylate ligands are bonded through carboxylate oxygen, which is the most common coordination mode of mono-deprotonated salicylic acid. The uncoordinated carbonyl C–O distances [C18–O3 = 1.250 (3) Å; C11–O6 = 1.244 (3) Å] in two carboxylate groups are slightly different from each other, due most probably to two strong intra-molecular hydrogen-bonding interactions between O3 (Table 2).

The crystal packing in **1** is formed by intermolecular hydrogen-bonding and π–π interactions (Fig. 2). Each neutral molecule unit is linked to a neighbor unit via hydrogen-bonding interactions through the solvate water and aqua molecules, N4 atom on the free pyridyl ring, and carboxylate O3 and

Table 2
Selected geometric parameters for **1** (Å,°)

Zn1–O2 1.9682 (19)	O2–Zn1–O5 105.70 (8)
Zn1–O5 2.007 (2)	O2–Zn1–O1 97.40 (9)
Zn1–O1 2.044 (2)	O2–Zn1–N1 113.75 (8)
Zn1–N1 2.081 (2)	O5–Zn1–N1 137.31 (8)
Zn1–N3 2.301 (2)	O1–Zn1–N1 93.37 (8)
C11–O6 1.244 (3)	O2–Zn1–N3 86.60 (8)
C18–O3 1.250 (3)	O5–Zn1–N3 94.74 (8)
N2–N3 1.250 (3)	O1–Zn1–N3 165.80 (8)
	N1–Zn1–N3 72.61 (7)

O6 atoms (see Table 3 for details). An intermolecular π–π contact occurs between the two symmetry-related salicylate rings (hereinafter ring A) of neighboring molecules. Ring A is oriented in such a way that the perpendicular distance from A to A^{iii} is 3.487 Å, the closest interatomic distance being C20···$C24^{iii}$ [3.545 (5) Å; symmetry code (iii) $2-x$, $1-y$, $1-z$]. The distance between the ring centroids is 3.736 (3) Å. There is also another π–π interaction between the symmetry related two coordinated pyridyl rings (Ring B) of neighboring molecules. Ring B is oriented in such a way that the perpendicular distance from B to B^{iv} is 3.527 Å, the closest interatomic distance being N1···$C2^{iv}$ [3.551 (4) Å; symmetry code: (iv) $2-x$, $1-y$, $-z$]. The distance between the ring centroids is 3.845 (3) Å. These are the most effective interactions that stabilize the crystal structure and form an infinite three-dimensional lattice.

3.2. Spectral characteristics

The electronic spectra of **1** and **2** in anhydrous THF at room temperature show intense bands in the UV region at 306 nm

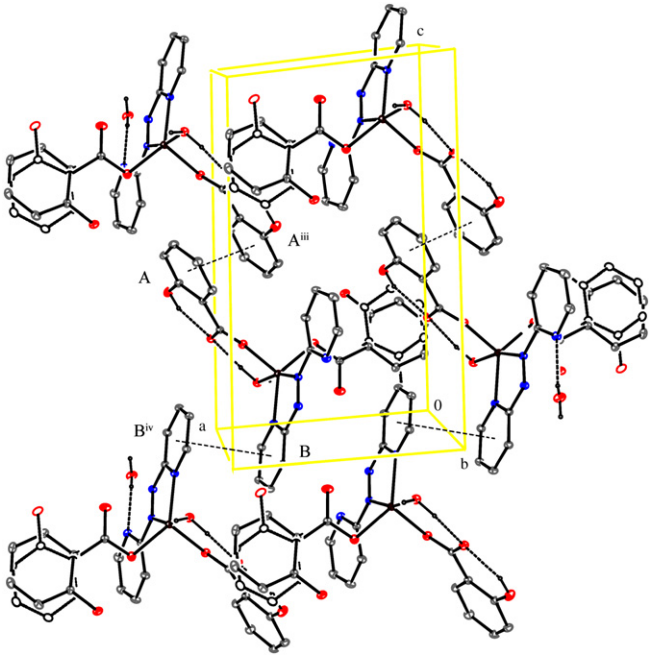


Fig. 2. The π–π interactions in **1** (dashed lines), with 10% probability displacement ellipsoids [symmetry codes: (iii) $2-x$, $1-y$, $1-z$, and (iv) $2-x$, $1-y$, $-z$].

Table 3
Hydrogen-bonding geometry for **1** (Å,°)

D–H···A	D–H	H···A	D···A	D–H···A
O1–H5··· O7i	0.79 (4)	1.88 (4)	2.666 (4)	169 (4)
O7–H12···O6^{ii}	0.75 (5)	2.08 (5)	2.826 (4)	175 (5)
O7–H11···N4	0.74 (4)	2.20 (4)	2.898 (4)	158 (4)
O1–H6···O3	0.93 (4)	1.87 (4)	2.702 (3)	147 (3)
O7–H11···N4	0.74 (4)	2.20 (4)	2.898 (4)	158 (4)

Symmetry codes: (i) $x, y-1, z$; (ii) $1-x, 1-y, -z$.

($\varepsilon = 19707$ L mol^{-1} cm^{-1}) and 306 nm ($\varepsilon = 33549$ L mol^{-1} cm^{-1}), respectively (Fig. 3). These bands have been assigned to $\pi \rightarrow \pi^*$ transitions of abpy ligand. The absorption spectra of the complexes also exhibit the bands in the visible region which are assigned as arising from MLCT transitions. These charge-transfer bands of **1** and **2** were observed at 456 nm ($\varepsilon = 304$ L mol^{-1} cm^{-1}) and 430 nm ($\varepsilon = 2329$ L mol^{-1} cm^{-1}), respectively. Both $\pi \rightarrow \pi^*$ transition and charge-transfer absorption bands of **2** are more broad and intense than **1**. The similar MLCT charge-transfer bands were observed in the various abpy complexes [6,22,23].

In the IR spectrum of **1**, the broad absorption band at 3600–2600 cm^{-1} was assigned to ν(O–H) vibrations of both water and phenol groups. The symmetric and asymmetric stretching modes of ν(COO) in salicylic acid appear at 1657 and 1394 cm^{-1}, respectively, while these vibration modes shift to lower frequencies (1587 and 1394 cm^{-1}) in **1** indicating the salicylic acid coordination to metal ion through the carbonyl oxygen [24]. The phenolic δ(OH) vibration at 1253 cm^{-1} in **1**, observed at 1305 cm^{-1} in free salicylic acid, clearly explains that the phenolic group is not deprotonated [25]. ν(N=N) vibration in abpy ligand of **1** is appeared at 1423 cm^{-1}.

3.3. Thermal behaviour

The thermal analysis curves (TG, DTA and DTG) of **1** are shown in Fig. 4. Thermal decomposition of **1** proceeds in four stages. The first stage is related to the dehydration and occurs in two steps in the 60–152 °C temperature range, accompanied by endothermic effects (DTG$_{max}$: 92, 123 °C). The weight loss (exp. 6.13%, calcd. 6.43%) corresponds to the loss of 1 mol coordinated water and 1 mol crystal water molecule. In second stage, **1** undergoes an exothermic phase transition at 189 °C. This transition is associated with a visual color change from brown to purple. The purple sample (**2**) does not revert to the original form when on keeping in atmosphere. The single crystallinity of **2** is observed to loose on phase transition. Therefore, we could not collect the intensity data of **2**. All structurally established coordination compounds of abpy have the ligand bonded to one or two metal centers via the azoimine (N=N–C=N) chelate arrangement. The conformation of the 2-pyridyl rings is another source of structural variety of abpy. The crystal structure analysis at the room temperature of **1** shows that free pyridyl-N atom is H-bonded with oxygen atom of crystal water (Fig. 1). Probably the H-bond network of **1** completely breaks down at around the phase transition temperature (189 °C) and the conformation of abpy ligand may be change from **IIa** to **IIb** conformation (Scheme 1). Third stage of **1** is related to the decomposition of the abpy and salicylato ligands by giving endothermic effects (DTG$_{max}$: 242 °C). In the fourth stage the strong exothermic peak of the DTA curve is associated with the burning of the organic residue. The final decomposition product, ZnO, was identified by IR spectroscopy. The overall weight loss (exp. 83.45%, calcd. 85.46%) agrees with the given structure.

4. Supplementary data

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as the supplementary publication no. CCDC 275406. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

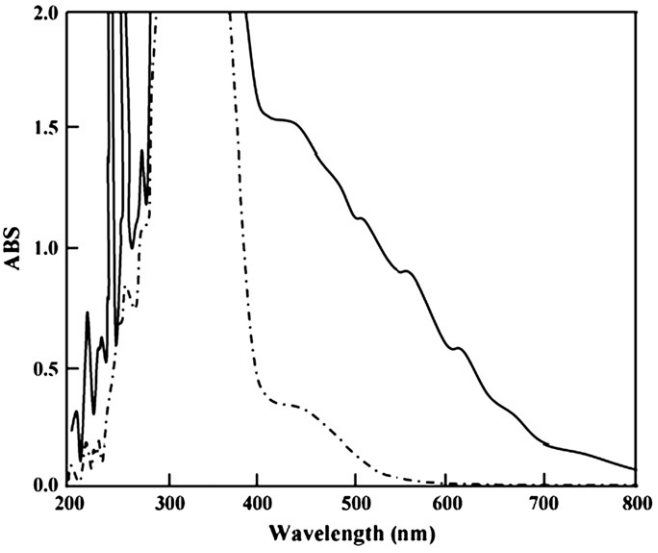


Fig. 3. UV–vis spectra of **1** (----) and **2** (-).

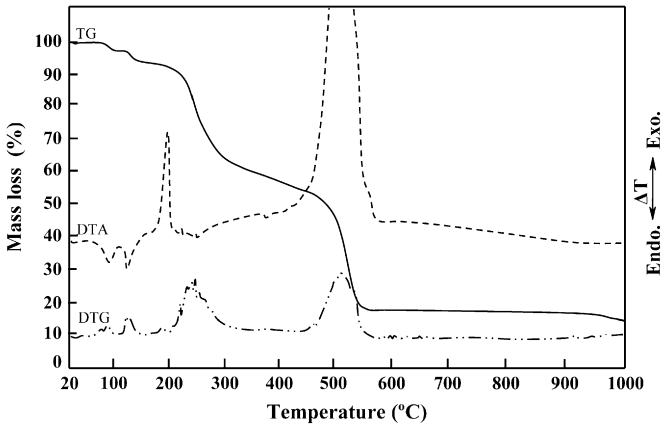


Fig. 4. TG, DTA and DTG curves of **1**.

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