

New complexes of 2-(4-pyridyl)-1,3-benzothiazole with metal ions; synthesis, structural and spectral studies

Małgorzata Kurzajewska, Dorota Kwiatek, Maciej Kubicki, Bogumił Brzezinski, Zbigniew Hnatejko*

Adam Mickiewicz University, Faculty of Chemistry, Umultowska 89b, 61-614 Poznań, Poland

ARTICLE INFO

Article history:

Received 9 November 2017

Accepted 25 March 2018

Available online 3 April 2018

Keywords:

Complexes

Coordination modes

2-(4-Pyridyl)-1,3-benzothiazole ligand

FT-IR and luminescence spectroscopy

X-ray structures

ABSTRACT

Reactions of the metal ions (Co(II), UO₂(II), Sm(III), Eu(III) and Zn(II)) with the 2-(4-pyridyl)-1,3-benzothiazole (*p*-PBT) and 2-(4-pyridyl)-1,3-benzothiazole N-oxide (N-O *p*-PBT) ligands lead to new complexes of the following types: [Co(*p*-PBT)₂(SCN)₂] (1), [Co(*p*-PBT)₂(dca)₂](MeOH) (2), [(*p*-PBT)₂Co{(μ-OAc)₂Co(*p*-PBT)₃}₂](PF₆)(CH₃OH) (3), [UO₂(*p*-PBT)(NO₃)₂] (4), [Sm(*p*-PBT)(Cl)₃(H₂O)₂·7H₂O] (5), [Eu(*p*-PBT)(bac)₃(H₂O)₂·4H₂O] (6), [Zn(*p*-PBT)₂(acac)₂] (7), [UO₂(*p*-PBT)(acac)₂] (8), [UO₂(N-O *p*-PBT)(acac)₂] (9). The structures of these complexes were characterized by elemental analysis, FT-IR spectroscopy and for 3, 7, 8, and 9 compounds by X-ray crystallography. The experimental data revealed that the metal ions are coordinated with the co-ligands via the N-, S- and O-donor atoms, whereas the *p*-PBT ligand coordinates exclusively through its pyridyl nitrogen atom. The photoluminescence properties of samarium and europium complexes were studied.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Benzothiazole (1,3-benzothiazole), composed of fused benzene and thiazole rings, is present in various natural or synthetic compounds which show interesting bioactivities [1]. Its derivatives, particularly interesting from the point of view of material science, are isomers of the pyridyl-benzothiazoles (*ortho*-, *meta*-, and *para*-PBT, Scheme 1). These compounds are prepared by condensation reaction of 2-aminothiophenol with the corresponding pyridine carboxylic acid [2], pyridine aldehyde [3] or pyridine ketone [4]. In recent years, many complexes of PBT with transition metal ions have been studied [5], however only a small number of reports have been concerned with *meta*- and *para*- isomers [3b,5f–g]. Obviously due to the steric demands, various coordination modes have been observed for different PBT isomers. In general, it has been found that *ortho*-PBT exhibits an N, N'-bidentate coordination mode, *meta*-PBT acts as single or bidentate ligand, while the *para*-PBT ligand coordinates with the metal ion exclusively through the nitrogen atom from the pyridine ring. Ternary complexes of metals ions with PBT isomers and some other ligands such as phenanthroline, β-diketones and amino acids have been also synthesized and characterized [6]. These compounds show interesting practical and biological properties. For instance, they are used as catalysts in hydrogenation of alkenes (I), in ring-open-

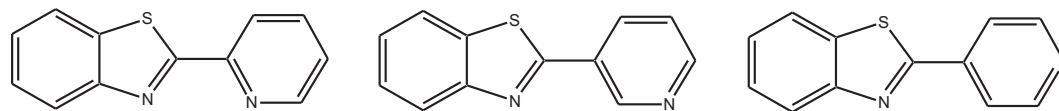
ing polymerization (II) and for electrochemical hydrogen production (III) [7]. They are also applied in electroluminescent devices [2b,6c]. The biological activity of these compounds is manifested by their interaction with DNA, cytotoxic activity and antibacterial properties [3a–c,5,6a–b,8].

Some authors have recently reported on the structure of Eu(III) complexes with β-diketones [6c,9]. Many of these complexes with cations of lanthanide (Ln) contain neutral nitrogen or oxygen donor ligands with coordination numbers 8, rarely 7 or 9. The lanthanide β-diketones have found widespread applications in the development of new materials such as sol–gel glasses, red-emitting electroluminescent devices, supramolecular assemblies or polymers [10].

Our study presented in this paper has been focused on *para*-PBT (*p*-PBT) ligand. Herein, we present detailed description of syntheses and physicochemical properties of new Co(II), UO₂(II), Sm(III), Eu(III) and Zn(II) complexes with the *p*-PBT ligand and co-ligands such as acetate (OAc), acetylacetonate (acac), benzoylacetonate (bac) and dicyanamide (dca, ⁻N(CN)₂). We also report the crystal structures of the complexes [(*p*-PBT)₂Co{(μ-OAc)₂Co(*p*-PBT)₃}₂](PF₆)(CH₃OH) (3), [Zn(PBT)₂(acac)₂] (7), [UO₂(*p*-PBT)(acac)₂] (8), [UO₂(N-O *p*-PBT)(acac)₂] (9) where β-diketone acts as a bidentate ligand and *p*-PBT as a monodentate ligand through N atom.

* Corresponding author.

E-mail address: zbychuh@amu.edu.pl (Z. Hnatejko).



Scheme 1. The *ortho*-, *meta*-, and *para*-PBT isomers.

2. Experimental

2.1. Syntheses

2-(4-pyridyl)-1,3-benzothiazole (*p*-PBT), 2-(4-pyridyl)-1,3-benzothiazole *N*-oxide (*N*-O *p*-PBT), Zn(acac)₂·H₂O, UO₂(acac)₂·H₂O and Eu(bac)₃·2H₂O compounds were synthesized according to the previously published methods [2a–b,11]. All other chemicals and solvents, used in our experiments, were commercially available and of analytical grade.

All newly obtained compounds are soluble in ethanol or acetonitrile solution.

2.1.1. [Co(*p*-PBT)₂(SCN)₂] (**1**)

The preparation of the (**1**) was performed as follows: 0.0530 g of *p*-PBT (0.25 mmol) was dissolved in methanol (15 mL). A solution of Co(CH₃COO)₂·4H₂O (0.0623 g; 0.25 mmol in 5 mL of methanol) and water/methanol (1:1, v:v) solution of NH₄SCN (0.0381 g, 0.5 mmol) were added dropwise to the *p*-PBT solution. The reaction mixture was refluxed at 40 °C for 3 h and then filtered. The pink precipitate was formed after few days. The precipitate was filtered, washed with ethanol and dried in air atmosphere. Yield: 0.0360 g (48%). *Anal.* Calc. for C₂₆H₁₆CoN₆S₄: C, 52.08; H, 2.69; N, 14.02; S, 21.39. Found: C, 52.15; H, 2.76; N, 13.97; S, 21.16.

2.1.2. [Co(*p*-PBT)₂(dca)₂]_n CH₃OH (**2**)

To a stirred solution of *p*-PBT ligand (0.0530 g, 0.25 mmol) in methanol (15 mL), a solution of Na[N(CN)₂] (0.0222 g, 0.25 mmol) in methanol (5 mL) was added dropwise. After that a methanol solution of Co(CH₃COO)₂·4H₂O (0.0623 g; 0.25 mmol) was added to the reaction mixture and the resulting pink mixture was stirred for 3 h at temperature of 40 °C. After filtration, the product was washed with methanol and then dried in air atmosphere. Yield: 0.1020 g (63%). *Anal.* Calc. for C₂₉H₂₀CoN₁₀O₅S₂: C, 53.78; H, 3.11; N, 21.63; S, 9.90. Found: C, 53.98; H, 3.26; N, 21.47; S, 10.01.

2.1.3. [(*p*-PBT)₂Co{(μ-OAc)₂Co(*p*-PBT)₃}₂](PF₆)(CH₃OH) (**3**)

A methanol solution of Co(CH₃COO)₂·4H₂O (0.0621 g, 0.25 mmol, 5 mL) was mixed with a solution (15 mL) of *p*-PBT (0.0533 g, 0.25 mmol) and NH₄PF₆ (0.0817 g, 0.5 mmol, 5 mL). The pink crystals X-ray quality precipitated after three weeks of decomposition on air. *Anal.* Calc. for C₁₀₅H₈₀Co₃F₆N₁₆O₉PS₈: C, 55.12; H, 3.52; N, 9.79; S, 11.21. Found: C, 55.24; H, 3.77; N, 9.73; S, 10.98%.

2.1.4. [UO₂(*p*-PBT)₂(NO₃)₂] (**4**)

Compound (**4**) was synthesized at temperature of 40 °C. A mixture of UO₂(NO₃)₂·6H₂O (0.1264 g, 0.25 mmol) and *p*-PBT (0.0531 g, 0.25 mmol) in acetonitrile solution (30 mL) was stirred for two hours until a yellow precipitate formed during stirring. The obtained product was washed with a small portion acetonitrile and then dried in air atmosphere. Yield: 0.1064 g (51%). *Anal.* Calc. for C₂₄H₁₆N₆O₈S₂U: C, 35.21; H, 1.97; N, 10.27; S, 7.83. Found: C, 35.56; H, 1.97; N, 10.11; S, 7.64%.

2.1.5. [Sm(*p*-PBT)(Cl)₃(H₂O)₂]·7H₂O (**5**)

To a stirred solution of *p*-PBT ligand (0.1062 g, 0.5 mmol) in acetonitrile (20 mL), a solution of SmCl₃·6H₂O (0.0912 g, 0.25 mmol) in 15 mL mixed solvent of water and acetonitrile (volume ratio

1:4) was added dropwise. The resulting mixture was intensively stirred and then filtered. The obtained product was washed a small amount acetonitrile and then dried in air atmosphere. *Anal.* Calc. for C₁₂H₂₆Cl₃N₂O₉SSm: C, 22.84; H, 4.15; N, 4.44; S, 5.08. Found: C, 22.95; H, 3.94; N, 4.44; S, 4.97%. Yield: 0.0902 g (57%) based on SmCl₃·6H₂O.

2.1.6. [Eu(*p*-PBT)(bac)₃(H₂O)]·4H₂O (**6**)

A methanol solution (20 mL) of Eu(bac)₃·2H₂O (0.0393 g, 0.06 mmol) was added dropwise to a methanol solution of *p*-PBT ligand (0.0265 g, 0.125 mmol, 5 mL) upon continuous stirring. The reaction mixture was stirred magnetically for 2 h. After a few days, the resulting light yellow precipitate was removed from the solution by suction and dried at room temperature. Yield: 0.1125 g (48%) based on Eu(bac)₃·2H₂O. *Anal.* Calc. for C₄₂H₄₅EuN₂O₁₁S: C, 53.79; H, 4.84; N, 2.99; S, 3.42. Found: C, 53.89; H, 4.94; N, 3.11; S, 3.17%.

2.1.7. [Zn(*p*-PBT)₂(acac)₂] (**7**)

p-PBT ligand (0.0532 g, 0.25 mmol) and Zn(acac)₂·H₂O (0.0709 g, 0.25 mmol) were dissolved in ethanol (20 mL) upon continuous stirring at 40 °C. The resulting solution was stirred for 3 h and then it was allowed to evaporate slowly at room temperature. After a few days, pale yellow single crystals were obtained, suitable for X-ray analysis. Yield: 0.0613 g (71%) based on *p*-PBT ligand. *Anal.* Calc. for C₃₄H₃₀N₄O₄S₂Zn: C, 59.34; H, 4.39; N, 8.14; S, 9.32. Found: C, 59.52; H, 4.64; N, 8.02; S, 9.14%.

2.1.8. [UO₂(*p*-PBT)(acac)₂] (**8**)

To a stirred solution of UO₂(acac)₂·H₂O (0.1223 g, 0.25 mmol) in ethanol (15 mL), a solution of *p*-PBT ligand (0.0530 g, 0.25 mmol) in 15 mL was added dropwise. The mixture was stirred and heated under reflux at 40 °C for 3 h. After one week, yellow crystals of [UO₂(*p*-PBT)(acac)₂] (X-ray quality) were obtained by slow evaporation of the solution at room temperature. Yield: 0.1143 g (67%). *Anal.* Calc. for C₂₂H₂₂N₂O₆SU: C, 38.83; H, 3.26; N, 4.12; S, 4.70. Found: C, 38.85; H, 3.44; N, 4.04; S, 4.57%.

2.1.9. [UO₂(*N*-O *p*-PBT)(acac)₂] (**9**)

This compound was prepared by following the procedure analogous to that mentioned above for (**8**) with UO₂(acac)₂·H₂O (0.1216 g, 0.25 mmol) and *N*-O *p*-PBT (0.0571 g, 0.25 mmol). Yellow crystals of the complex suitable for X-ray diffraction analysis were obtained. Yield: 0.1030 g (59%). *Anal.* Calc. for C₂₂H₂₂N₂O₇SU: C, 37.94; H, 3.18; N, 4.02; S, 4.60. Found: C, 37.75; H, 3.66; N, 3.97; S, 4.67%.

2.2. FT-IR, thermogravimetric and photoluminescence measurements, elemental analyses

The FT-IR spectra were recorded for the samples in the form of KBr pellets on a Jasco FT/IR-4200 spectrometer and are reported in cm⁻¹.

Thermogravimetric studies of selected polycrystalline samples were performed on a Setaram Setsys TG-DSC 12 thermal analyzer. Thermal characterization of the investigated compounds was made upon decomposition of the samples in air atmosphere at a heating rate of 5 °C/min.

Download English Version:

<https://daneshyari.com/en/article/7762720>

Download Persian Version:

<https://daneshyari.com/article/7762720>

[Daneshyari.com](https://daneshyari.com)