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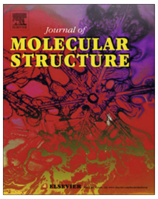

(1-Methyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole) and its three copper complexes: Synthesis, characterization and fluorescence properties

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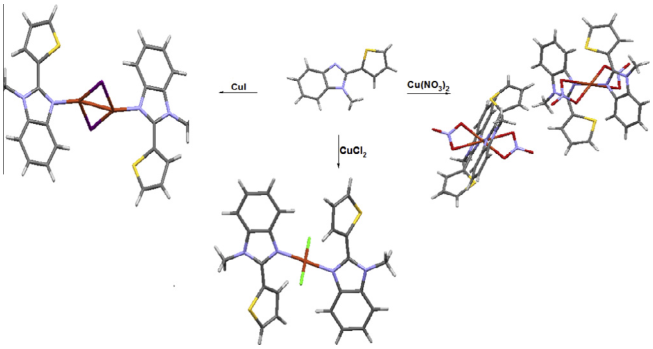
HIGHLIGHTS

- A new thiophene-substituted benzimidazol ligand, ($C_{12}H_{10}N_2S$; **L**), was synthesized.
- [(Cu_2(**L**)$_2I_2$], [(Cu(**L**)$_2X_2$] (X = Cl^-, and NO_3^-) were synthesized and structurally characterized.
- Ligand **L** emits blue fluorescence.
- [(Cu_2(**L**)$_2I_2$] complex shows poor yellow–green emission.

GRAPHICAL ABSTRACT



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ABSTRACT

(1-Methyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole) ($C_{12}H_{10}N_2S$) (**L**) ligand and its three copper complexes [(Cu_2(**L**)$_2I_2$] (**1**), [(Cu(**L**)$_2X_2$] (X = Cl^- (**2**), and NO_3^- (**3**)) were synthesized and characterized by elemental analysis and IR measurements. The structures of the complexes **1–3** were determined by single crystal X-ray diffraction. The complex molecules interact with each other's via weak C—H···X hydrogen bonds (X = I for the complex **1**, X = Cl for the complex **2** and X = O for the complex **3**). Upon excitation with a wavelength of 350 nm at room temperature, free **L** and complex **1** emit fluorescence at 420 and 560 nm, respectively.

Introduction

In recent years, increasing attention has been given to the chemistry of copper complexes and clusters not only for their structures and topologies, but also for their attractive magnetic and biological properties, mixed-valance oxidation-state pairs, and potential applications such as dye-sensitized solar cells (DSSCs) [1–5]. Furthermore, because of the d^{10} electronic configuration of copper(I) ions which diversifies luminescent behavior, growing interest has been given to the photophysical and photochemical properties of copper(I) complexes [6–15].

Benzimidazole- or imidazole-containing ligands can easily coordinate to metal ions, as well as act as hydrogen-bond acceptors

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or donors in reactions and thus their coordination chemistry has been extensively investigated [16–23]. Metal ions play a vital role in a vast number of widely different biological processes. The interaction of these ions with biologically active ligands, for example in drugs, is a subject of interest. One of the most attractive features of benzimidazole ligands in the field of biological investigations have been their structural similarities with the common purine type nucleobases. Since the use of cisplatin, $[Pt(NH_3)_2Cl_2]$ as an effective anticancer drug, the interest toward transition metal complexes containing N-donor ligands has increased in order to obtain metal-based drugs exhibiting a high biological activity together with a reduced toxicity [17,18]. In this respect, benzimidazole derivatives together with their metal complexes such as Pt(II), Fe(II), Cd(II), Hg(II), Co(II), Cu(II), and Zn(II) have been investigated and found to display various biological activities [19–22]. In addition, benzimidazole-based organic ligands and their metal complexes continue to attract interest as components in catalytic systems [21] and luminescent materials [23].

In the view of these facts, we believed it would be valuable to synthesize new benzimidazole-based ligand and complexes useful for some medical and photochemical applications. Herein we present the results of the synthesis and characterization of (1-methyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole) (**L**) and its copper complexes $[(Cu_2(\mathbf{L})_2I_2]$ (**1**), $[(Cu(\mathbf{L})_2X_2]$ ($X = Cl^-$ (**2**), and NO_3^- (**3**)). The complexes were characterized by single crystal X-ray diffraction, elemental analysis, and IR measurements. Furthermore, the luminescent properties of the **L** and of the complexes were also investigated.

Experimental

Materials and methods

All reagents and solvents used were of analytical grade. Reactions under microwave irradiation were performed in a modified domestic microwave oven (Bosch HMT 812C). Reactions were monitored by thin-layer chromatography (TLC) on silica-gel 60 F254 plates (Merck) and an UV lamp. The melting point was determined using a capillary tube and a digital melting point apparatus (Gallenkamp Electrothermal). The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avence II-400 MHz NMR spectrometer using TMS as an internal standard and DMSO-d_6 as solvent. IR spectra were recorded on a Perkin–Elmer 100 FTIR spectrophotometer as ATR between 4000 and 650 cm^{-1}. The elemental analyses (C, H, N and S contents) were determined with a LECO, CHNS-932 instrument. Fluorescence spectra of the solid samples and electronic spectra of the **L** and complexes in DMSO at room temperature were recorded on Molecular Devices Spectra M5 fluorescence spectrophotometer.

*Synthesis of **L** and its complexes*

*Synthesis of the ligand **L**, (1-methyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole)*

1-Methyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole was synthesized by condensation of N-methyl-1,2-phenylenediamine with bisulfite adduct of 2-thiophenecarboxaldehyde under neat microwave conditions as previously described [24]. Briefly, 2-thiophenecarboxaldehyde 4.57 g (40 mmol) was dissolved in 20 ml ethanol and $NaHSO_3$ 4.16 g (40 mmol) in 20 ml water was added in portions. The mixture was stirred vigorously for one hour in an ice bath. The precipitate was bisulfite adduct of 2-thiophenecarboxaldehyde, filtered as white solid and dried under vacuum (4.4 g, yield: 50%). 1 mmol (0.12 g) of N-methyl-1,2-phenylenediamine and 1 mmol (0.22 g) of bisulfite adduct of 2-thiophenecarboxaldehyde were mixed. After adding a few drops of dimethylformamide, the mixture was irradiated in a modified domestic microwave oven for 8 min until the reaction was completed according to the TLC (chloroform/methanol: 9/1) data. The mixture was cooled and poured into ice cold water under vigorous stirring. The precipitate was collected by filtration, washed with water and crystallized from methanol/water. Light brown crystals were obtained (0.16 g, yield 77%). The synthesis procedure of 1-methyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole is shown in Scheme 1.

IR (υ, cm^{-1}): 3098 m (C—$H_{arom.}$); 2947m (CH_3); 1644s (C=N); 1612m, 1558s, 1459vs, 1443vs (C=C); 1389m, 1287s (C—N); 848s, 746s (C—S). ^1H NMR (400 MHz, DMSO-d_6): δ 2.49 and 3.39 (solvent peaks), 4.00 (s, 3H, NCH_3), 7.20–7.24 (m, 1H, thiophene-H), 7.25–7.29 (m, 2H, Ar—H), 7.62 (m, 2H, Ar—H), 7.80–7.77 (m, 2H, thiophene-H). ^{13}C NMR (400 MHz, DMSO-d_6): δ 32.0, 110.85, 119.14, 122.61, 122.95, 128.61, 128.84, 129.76, 132.99, 137.06, 142.70, 147.74.

Synthesis of the complexes

$[Cu_2(\mathbf{L})_2I_2]$, (**1**): A 20 mL methanolic solution of CuI (0.0476 g, 0.25 mmol) was mixed with KI (0.85 g, 5.12 mmol) with stirring at 60 °C. Into the resulting clear solution, (0.0535 g, 0.25 mmol) **L** in 5 mL methanol added. Single crystals of **1** were obtained within a few days after filtration of precipitate. 0.066 g of the product was obtained (yield 65%, based on **L**). Anal. Calc. for $C_{24}H_{20}$ $I_2N_4S_2Cu_2$ (809.54 g, 7 mol): C, 35.60; H, 2.47; N, 6.92%; S, 7.92%. Found C, 34.90; H, 2.53; N, 7.06%; S, 7.51%. IR (υ, cm^{-1}): 3095m, 3045m (C—$H_{arom.}$); 2935w (CH_3); 1613m (C=N); 1557s, 1480s, 1461vs, 1447s (C=C), 1326, 1229 (C—N); 846s, 746s (C—S).

$[Cu(\mathbf{L})_2Cl_2]$, (**2**): Single crystals of the complex **2** were obtained by mixing 0.034 g $CuCl_2$, **L** (0.033 g) and succinic acid ($sucH_2$, 0.029 g) in 5 mL DMF/1 mL water at 60 °C. M: $SucH_2$: **L** ratios are 1:1:2 mmol.

Bulk synthesis: **L** (0.0535 g, 0.25 mmol) and $CuCl_2$(0.0338 g, 0.25 mmol) were mixed in 10 mL methanol at 60 °C for 30 min. The pale green precipitate was filtered off and dried in air (0.05 g, yield: 71%, based on **L**). Anal. Calc. for $C_{24}H_{20}Cl_2N_4S_2Cu$ (563 g/mol): C, 51.20; H, 3.55; N, 9.95%; S, 11.39%. Found C, 49.89; H, 3.59; N, 10.04%; S, 11.19%.

IR (υ, cm^{-1}): 3084m, 3055vs (C—$H_{arom.}$), 2935w (CH_3), 1609s (C=N), 1555s, 1473s, 1460s, 1448s (C=C), 1336m, 1232s (C—N); 850s, 750s (C—S).

$[Cu(\mathbf{L})_2(NO_3)_2]$, (**3**): $Cu(NO_3)_2{\cdot}3H_2O$ (0.0602 g, 0.25 mmol) and **L** (0.0535 g, 0.25 mmol) were refluxed for 1 h in 10 mL methanol and vacuum-filtered. The remaining solution was left undisturbed for crystallization (0.014 g, yield 18%, based on **L**). Anal. Calc. for $C_{24}H_{20}N_6S_2O_6Cu$ (679.73 g/mol): C, 42.41; H, 2.94; N, 12.36%; S, 9.43%. Found C, 45.65; H, 3.33; N, 13.90%; S, 10.42%.

IR (υ, cm^{-1}): 3096m (C—$H_{arom.}$); 2957m (CH_3); 1613w (C=N); 1559s, 1450vs (C=C); 1331m, 1233m (C—N); 855s, 744s (C—S); 1676w, 1464vs, 1280vs, 1014s, 717vs (NO_3^-).

X-ray diffraction studies

Full data collection of single crystal was carried out on a Bruker Quest D8 device with microfocus Mo Kα radiation and Photon 100 CMOS detector. Very weak *h0l* reflections with odd $h + l$ were detected for **1**, but it was not possible to determine reliable intensities. Therefore an average structure was described in the further stages of structure determination, limiting its accuracy. The investigated crystal of **2** was twinned with two twin domains at ~74:26 ratio. Reflections belonging to different twin domains were identified and a twin data integration/reduction was performed [25]. For further structure solution and refinement only data from the major (~74%) twin domain were taken. Selected crystallographic data are