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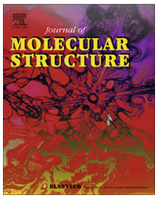

(1-Methyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole) and its three copper complexes: Synthesis, characterization and fluorescence properties

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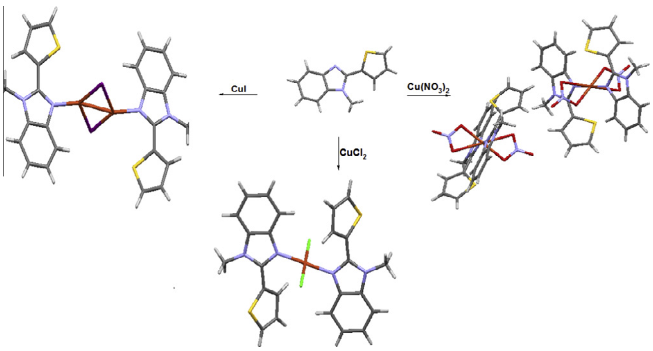
HIGHLIGHTS

- A new thiophene-substituted benzimidazol ligand, ($C_{12}H_{10}N_2S$; **L**), was synthesized.
- $[(Cu_2(\mathbf{L})_2I_2]$, $[(Cu(\mathbf{L})_2X_2]$ ($X = Cl^-$, and NO_3^-) were synthesized and structurally characterized.
- Ligand **L** emits blue fluorescence.
- $[(Cu_2(\mathbf{L})_2I_2]$ 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 $[(Cu_2(\mathbf{L})_2I_2]$ (**1**), $[(Cu(\mathbf{L})_2X_2]$ ($X = Cl^-$ (**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.

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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%.

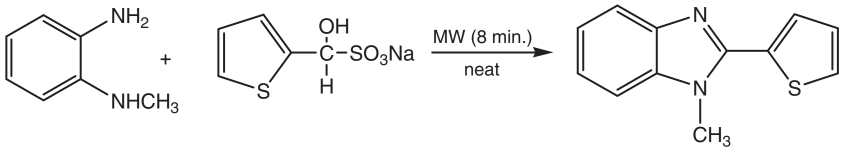
IR (υ, cm^{-1}): 3084m, 3055vs (C—H$_{arom.}$), 2935w (CH_3), 1609s (C=N), 1555s, 1473s, 1460s, 1448s (C=C), 1336m, 1232s (C—N); 850s, 750s (C—S).

$[Cu(\mathbf{L})_2(NO_3)_2]$, (**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



Scheme 1. Synthesis of the 1-methyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole ligand.

Table 1
Selected X-ray data for **1–3**.

	1	**2**	**3**
Formula	$C_{24}H_{20}Cu_2I_2N_4S_2$	$C_{24}H_{20}Cl_2CuN_4S_2$	$C_{24}H_{20}CuN_6O_6S_2$
Formula weight	809.44	563.00	616.12
Temperature (K)	100(2)	100(2)	100(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.580 (2)	7.204 (3)	9.306 (4)
b (Å)	15.035 (3)	9.230 (3)	11.690 (5)
c (Å)	9.594 (2)	9.505 (4)	12.206 (6)
α (°)		89.09 (3)	97.56 (2)
β (°)	112.49 (3)	89.49 (3)	106.96 (2)
γ (°)		67.61 (3)	94.24 (2)
V (Å^3)	1276.8 (5)	584.3 (4)	1250 (1)
Z, ρ_{calc} (g cm^{-3})	2, 2.105	1, 1.600	2, 1.637
μ (mm^{-1})	4.27	1.36	1.10
F(000)	776	287	630
Crystal size (mm)	0.22 × 0.07 × 0.06	0.35 × 0.07 × 0.07	0.12 × 0.08 × 0.04
θ range (°)	2.56–25.00	2.14–25.00	2.30–25.00
rflns: total/unique	17,527/2241	9288/1976	19,932/4394
R(int)	0.032	0.081	0.047
Abs. corr.	Numerical	Numerical	Numerical
Min., max. transmission factors	0.578, 0.867	0.708, 0.927	0.578, 0.867
Data/restraints/params	2241/0/130	1976/0/152	4394/1/351
GOF on F^2	1.01	1.02	1.01
$R1$ [$I > 2\sigma(I)$]	0.040	0.030	0.035
wR_2 (all data)	0.104	0.088	0.108
Max., min. $\Delta\rho_{elect}$ [e Å^{-3}]	2.49, −0.81	0.31, −0.51	0.82, −0.38

given in Table 1. **1**, **2** and **3** were solved by direct methods in SHELXS and refined in SHELXL97 [26]. All H atoms positions were calculated and constrained with $U_{eq} = 1.5/1.2U_{eq}$(parent C atom) for methyl/aromatic H atoms, respectively.

1: As a result of problems with refinement of the C atoms displacement parameters an EADP restraint was used for the C4 and C5 atoms. On the final difference Fourier map the highest maximum of 2.49 e/Å^3 is located 0.36 Å from C4. These problems could not be resolved with any disorder model and might be connected with averaging of this structure. Therefore no detailed discussion of structure parameters will be undertaken.
2: On the final difference Fourier map the highest maximum of 0.31 e/Å^3 is located in the middle of C8—S1 bond (0.68 Å from C8, 1.07 Å from S1).
3: One thienyl ring is probably slightly continuously disordered. As a result, SADI restraints were used for C91—C81 and C91—C101 bond lengths and EADP restraints were applied to C81, C91 atoms. On the final difference Fourier map the highest maximum of 0.82 e/Å^3 is located on the C91—C101 bond.

Results and discussion

While we are trying to synthesize metal–organic frameworks, containing policarboxylic acids such as succinic, fumaric acid and 1,4-benzenedicarboxylic acids and **L** in DMF/water solution, we obtained the single crystals of the complex **2** from the solution of succinic acid. Probably because of the high pK_a values of the fumaric and 1,4-benzenedicarboxylic acids, their solutions gave low quality crystals which were not suitable for single crystal data collection due to fast crystallization. The colors of the compounds confirm the oxidation state of the metal centers. Because of d^{10} electron configuration of the Cu$^+$, no d–d transition occurs in the compound **1** and it is colorless. On the other hand, the compounds **2** and **3** are green–blue because of Cu^{2+} oxidation state.

Infrared spectra

The infrared spectral data for the free ligand and the complexes are presented in the experimental section (for IR spectra see supplementary figures). When the IR spectra of the free ligand and the complexes are compared, some characteristic changes are observed. The C—H stretching modes of the aromatic ring and the CH_3 group of the ligand were observed in the regions of 3000 cm^{-1}, as expected. Another characteristic region of the spectrum of benzimidazole derivatives is 1500–1650 cm^{-1} which can be attributed to C=N and C=C stretching vibrations. The free ligand shows a strong absorption band at 1644 cm^{-1} that is due to the stretching vibration of the C=N of the imidazole ring [27,28]. In the IR spectra of all complexes this stretching band is apparently shifted to lower frequencies (1613–1609 cm^{-1}) with a reduced intensity, suggesting that the imine nitrogen of the benzimidazole is effectively coordinated to the metal ion [29].

A pair of strong bands in the 1612–1443 cm^{-1} region of the free ligand were assigned to the overall C=C ring-skeletal (benzimidazole and thiophene moieties) stretching vibrations [30]. Additionally, the ligand shows characteristic absorption bands at 1389 and 1287 cm^{-1} due to the C—N stretchings of the imidazole ring and

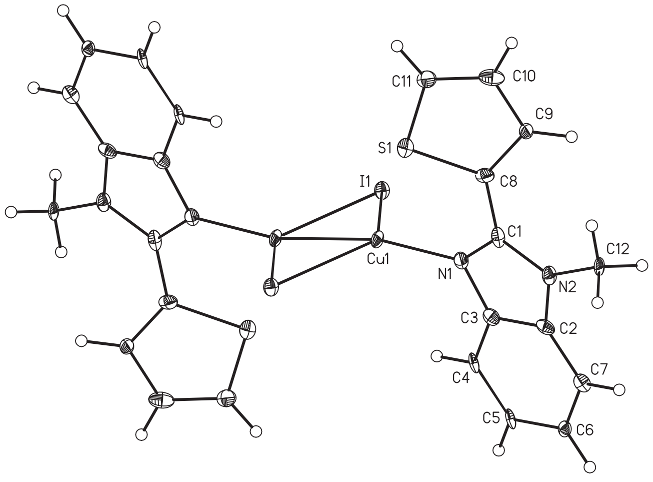


Fig. 1. Molecular structure of the complex **1**. Thermal ellipsoids are plotted at 30% probability level. Symmetry-independent part is labeled.

Table 2
Selected geometric parameters (Å, °) for **1**, **2** and **3**.

1			
Cu1—N1	1.981 (6)	Cu1—I1	2.5835 (11)
Cu1—I1^{i}	2.5770 (10)		
N1—Cu1—Cu1^{i}	165.01 (18)	Cu1^{i}—Cu1—I1	60.00 (4)
N1—Cu1—I1^{i}	120.75 (16)	I1^{i}—Cu1—I1	120.25 (3)
Cu1^{i}—Cu1—I1^{i}	60.25 (3)	Cu1^{i}—I1—Cu1	59.75 (3)
N1—Cu1—I1	116.81 (17)		
Symmetry codes: (i) −x+1, −y, −z+2			
2			
Cu1—N1	1.9583 (19)	N1—C3	1.393 (3)
Cu1—Cl1	2.2824 (10)	N2—C1	1.358 (3)
S1—C11	1.710 (3)	N2—C2	1.390 (3)
S1—C8	1.723 (2)	N2—C12	1.464 (3)
N1—C1	1.333 (3)		
N1—Cu1—N1^{i}	179.999 (1)	C1—N1—Cu1	125.70 (15)
N1—Cu1—Cl1	90.95 (6)	C3—N1—Cu1	128.27 (15)
N1—Cu1—Cl1^{i}	89.05 (6)	C1—N2—C2	107.26 (17)
C11—S1—C8	91.53 (12)	C1—N2—C12	127.29 (19)
C1—N1—C3	106.03 (17)	C2—N2—C12	125.35 (18)
Symmetry codes: (i) −x+1, −y+1, −z+1			
3			
Cu1—N1	1.973 (2)	Cu1—O5	2.590 (3)
Cu1—O2	2.123 (3)	Cu2—O4	2.005 (2)
Cu1—O1	2.373 (3)	Cu2—N4	1.971 (2)
N3—O1	1.249 (3)	N6—O4	1.296 (3)
N3—O2	1.276 (3)	N6—O5	1.239 (3)
N1—Cu1—N1^{i}	179.999 (1)	N1—Cu1—O1^{i}	88.72 (9)
N1—Cu1—O2^{i}	88.68 (9)	N1^{i}—Cu1—O1^{i}	91.28 (9)
N1^{i}—Cu1—O2^{i}	91.32 (9)	O2^{i}—Cu1—O1^{i}	56.96 (8)
N1—Cu1—O2	91.32 (9)	O2—Cu1—O1^{i}	123.04 (8)
N1^{i}—Cu1—O2	88.68 (9)	N4—Cu2—N4^{ii}	180.00 (14)
N1—Cu1—O1	91.28 (9)	N4—Cu2—O4^{ii}	88.89 (9)
N1^{i}—Cu1—O1	88.72 (9)	N4^{ii}—Cu2—O4^{ii}	91.11 (9)
O2^{i}—Cu1—O1	123.03 (8)	N4—Cu2—O4	91.11 (9)
O2—Cu1—O1	56.96 (8)	N4^{ii}—Cu2—O4	88.89 (9)
Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x, −y+2, −z			

Table 3
Weak hydrogen bonding parameters (Å, °) for **1**, **2** and **3**.

D—H···A	D—H	H···A	D···A	D—H···A
1				
C12—H12B···Cl1^{i}	0.98	2.77	3.719 (3)	163
C11—H11···Cl1^{ii}	0.95	2.68	3.624 (3)	176
Symmetry codes: (i) x, y+1, z; (ii) −x+1, −y+1, −z				
2				
C7—H7···I1^{i}	0.95	3.21	4.130 (3)	165
C12—H12B···I1^{ii}	0.98	3.32	3.924 (7)	122
Symmetry codes: (i) x+1, y, z+1; (ii) x+1/2, −y+1/2, z+1/2				
3				
C41—H41···O1^{i}	0.95	2.60	3.140 (4)	117
C71—H71···O2^{ii}	0.95	2.59	3.352 (4)	138
C91—H91···O6	0.95	2.43	3.272 (4)	148
C42—H42···O4^{iii}	0.95	2.59	3.134 (4)	117
C72—H72···O6^{iv}	0.95	2.52	3.369 (4)	149
C92—H92···O3	0.95	2.57	3.136 (4)	118
Symmetry codes: (i) −x+1, −y+1, −z+1; (ii) −x, −y+1, −z+1; (iii) −x, −y+2, −z; (iv) x+1, y, z				

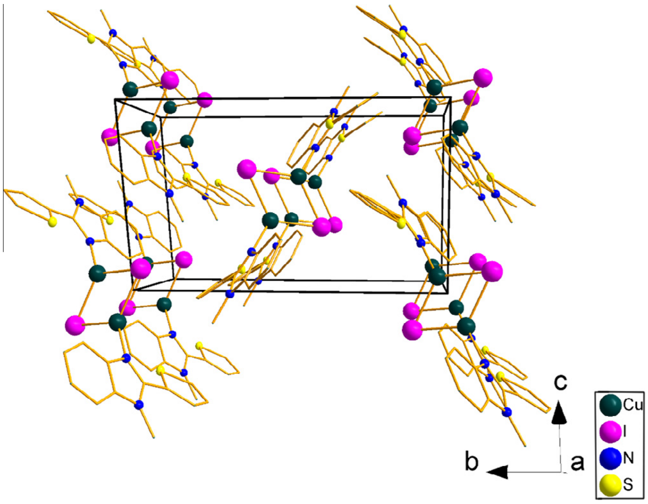


Fig. 2. Stacks of the $[Cu_2I_2]$ units along [1 0 0] formed in **1**. H atoms are omitted, C atoms are shown as sticks for clarity.

strong bands at 848 and 746 cm^{-1}, assigned to the C—S stretching vibration of the thiophene ring [31]. All these bands in the spectra of all complexes were similar to those in the corresponding ligand spectrum, except for slight shifts in their positions and changes in their intensities due to coordination.

Due to no experimental access to the spectral range below 600 cm^{-1} the Cu—Cl, Cu—I and Cu—N bond stretching bands, typically located below 400 cm^{-1}, could not be identified in the spectra of the complexes. Additionally, for the complex **3**, very strong bands at 1464, 1280, 1014 and 717 cm^{-1} originated from the O—NO_2 stretching modes, obviously confirm the presence of a coordinated nitrate group [32–35]. The small splitting (9 cm^{-1}) of the in-plane bending nitrate vibrations at 717 and 708 cm^{-1} may be indicative of the presence of a monodentate nitrate group [33–35].

Description of the crystal structures

The structures of the ligand **L** and its metal complexes have not been reported [36].

*[Cu_2(**L**)$_2I_2$], (**1**)*

1 comprises discrete centrosymmetric binuclear $[Cu_2I_2]$ units bridged by two iodine ligands (Fig. 1). The coordination sphere of each Cu^+ ion is completed with one N-coordinated **L** ligand. The geometric parameters of the central dumbbell $[Cu_2I_2]$ motif with Cu—I bond lengths at 2.577(1)–2.584(2) Å and acute Cu—I—Cu bond angle of 59.75(3)° are in agreement with the values reported for analogous compounds [37–39] (Table 2). The Cu···Cu distance within each unit is of 2.570(2) Å, which is a typical value [37–

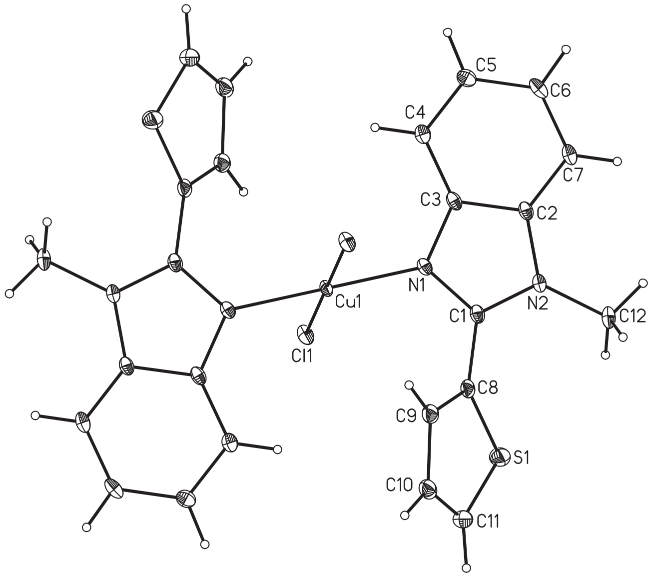


Fig. 3. Molecular structure of complex **2**. Thermal ellipsoids are plotted at 30% probability level. Only non-hydrogen atoms are labeled. Non-labeled part is generated by a symmetry operation 1−*x*, 1−*y*, 1−*z*.

39], similar to that reported for the Cu metal (2.56 Å; [39]). The Cu—N bond lengths are typical for comparable $[Cu_2I_2]$ units and N-coordinated imidazole derivatives [37–39]. As a result of the symmetry centre located in the middle of the $[Cu_2I_2]$ unit the corresponding aromatic rings of the two **L** ligands are parallel. Within each ligand the thienyl and benzimidazole rings planes are twisted with respect to each other by 26.7(3)°. N-methyl groups and benzimidazole C atoms are involved as donors in weak C—H···I hydrogen bonds (Table 3) to create a 3D-network. The $[Cu_2I_2]$ units form stacks extending along [100] with an intercentroid distance of ~9.58 Å (Fig. 2).

*[Cu(**L**)$_2$Cl$_2$], (**2**)*

2 is a mononuclear copper(II) complex containing two **L** molecules and two chlorine ligands per copper(II) centre. In each neutral centrosymmetric complex molecule in **2** (Fig. 3) the central Cu^{2+} ion coordination environment is planar quadratic with two chlorine ligands *trans* to each other and two organic ligands coordinated monodentately through benzimidazole N atoms. An analogous complex with **L** ligand (differing from **L** by the absence of an N-methyl substituent), in form of ethanol solvate, was reported by Belicchi et al. [40]. It is interesting to note that this related complex differs with respect to **2** by rotation of the thienyl ring, which thus is involved in a short contact to the central Cu^{2+} ion – in the molecule of **2** this is sterically impossible. Geometric parameters of the Cu^{2+} ion coordination sphere in **2** and the selected bond lengths/angles of the organic ligand are listed in Table 2. The Cu—N/Cl bond lengths are within the reported range [40]. In the organic ligand **L** molecule the N1—C1 bond involving the benzimidazole N atom coordinated to the Cu^{2+} ion is slightly longer than the N2—C1 bond involving the N-methyl-substituted N atom (Table 2). The C—S bond lengths within the thienyl ring are equivalent (Table 2). The interplanar angle between the plane of the benzimidazole ring and the plane of the thienyl ring is of 43.9(1)°.

The complex molecules in **2** interact through bifurcated weak C—H···Cl hydrogen bonds (Table 3) [41], involving thienyl ring/methyl group C atoms as donors. Thus hydrogen-bonded layers parallel to (011) are formed (Fig. 4).

*[Cu(**L**)$_2$(NO$_3$)$_2$], (**3**)*

3 is a mononuclear copper(II) complex with two **L** ligands and two nitrate ligands forming *trans*-arranged pairs in the coordination sphere of the Cu^{2+} ion (Fig. 5). There are two symmetry-inde-

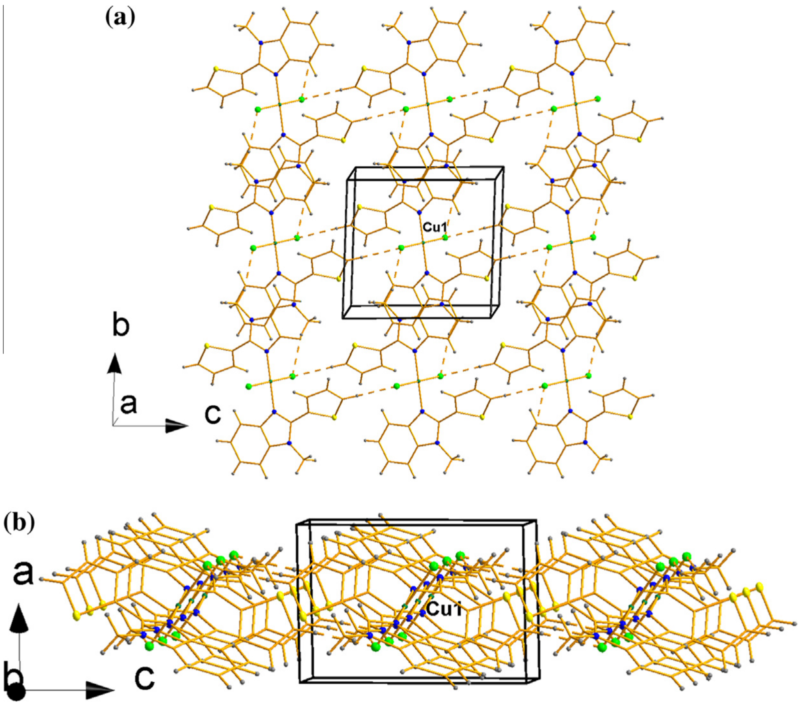


Fig. 4. Layers stabilized by weak C—H···Cl hydrogen bonds (dashed lines) in **2**, two different views (a and b). C atoms are shown as sticks for clarity.

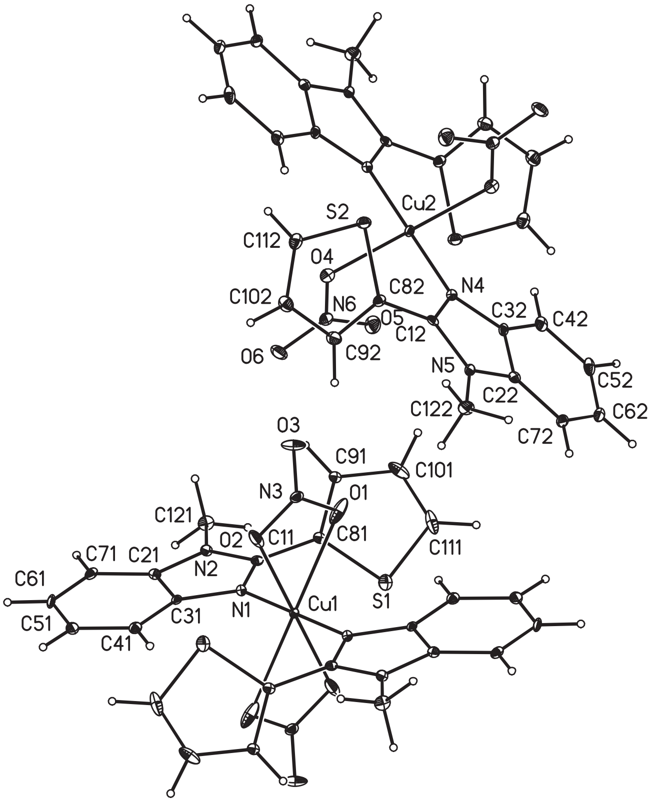


Fig. 5. Molecular structure of the complex **3**. Thermal ellipsoids are plotted at 30% probability level. Symmetry-independent part is labeled.

pendent centrosymmetric complex molecules significantly differing with geometric parameters. The most striking difference concerns coordination of the nitrate ligands. In both cases they are asymmetrically coordinated with different Cu—O bond lengths. In the Cu1-molecule these bond lengths are 2.373(3) and 2.123(3) Å, whereas in the Cu2-molecule they are 2.005(2) and 2.590(3) Å, respectively. Therefore the nitrate ligand in the Cu2-molecule should be regarded as quasi-monodentate with one semi-coordination bond. The shorter Cu—O bonds correspond to prolonged N—O bonds in the coordinating nitrate ligand (Table 2). Similar effect is observed in related compounds containing nitrate ligands coordinated to the Cu^{2+} ions [33]. Moreover, the Cu···S contacts involving the **L** thienyl rings are slightly different with shorter Cu1···S1 distance of 3.470(2) Å and longer Cu2···S2 distance of 3.507(2) Å. At the same time the Cu—N bonds involving the ligand benzimidazole N atom are equivalent. The differences in the molecular geometry of the two symmetry-independent molecules cannot be correlated with intermolecular interactions, which are weak and with similar pattern for both molecules (Table 3) and might be attributed to a dynamic Jahn–Teller effect [33–35].

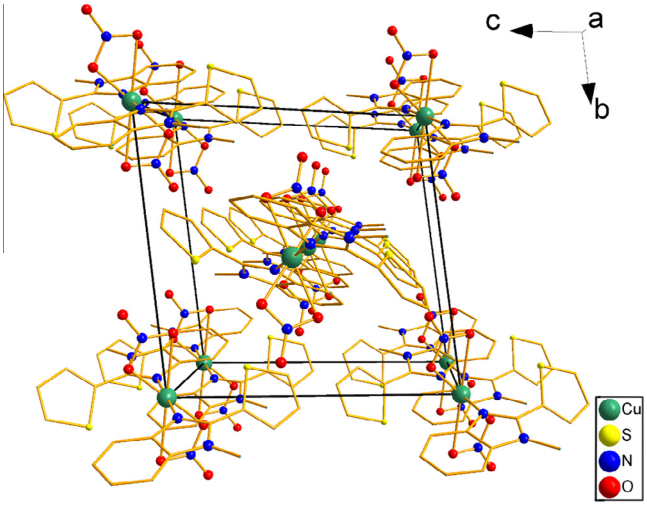


Fig. 6. Layered arrangement of the complex molecules in **3** with columns defined along [1 0 0]. H atoms are omitted and C atoms are shown as sticks for clarity.

Interplanar angles between the benzimidazole and thienyl rings in the **L** ligands in the two molecules are similar, adopting 46.1(1) and 44.2(1)° values for the Cu1- and Cu2-containing molecules, respectively. However, the relative arrangement of the nitrate and **L** ligands is different as evidenced by the corresponding interplanar angles. For the benzimidazole vs nitrate planes these are 90.0(1) and 79.4(1)°, for the nitrate and thienyl planes 47.9(2) and 37.5(2)° for the Cu1- and Cu2-containing molecules, respectively.

The complex molecules in **3** are arranged in layers parallel to (1 0 1), interconnected by weak C—H···O hydrogen bonds (Table 3) to form a 3D hydrogen bonding network. Moreover, columns of the complex molecules can be defined along [1 0 0] (Fig. 6).

Fluorescent properties

The electronic spectra of the **L** and the complexes which recorded in DMSO are given in the Supp. Fig. 7. The **L** and the complexes show two bands at *ca.* 280 and 350 nm attributed to the intra-ligand transitions of the **L**. The broad bands in the region 700–950 nm are assigned to the *d*–*d* transitions of the complexes **2** and **3**.

Supp. Fig. 8 shows the solid state fluorescent spectra of the **L** with the excitation wavelengths of 300, 310, 320, 330, 340 and 350 nm at room temperature. The solid state fluorescent spectra of the **L** and the complex **1** which were recorded with an excitation wavelength of 350 nm are shown in Fig. 7. Free **L** emits intense fluorescence at 420 nm upon excitation; however the intensity of the emissions is quenched by the complex formation. It is known that the luminescence in the first-row transition metal complexes is often bypassed by the presence of lowlying ligand-field excited states probably because of too short-lived to have measurable emissions. However, filled-shell d^{10} systems offer an opportunity to observe other excited states [7]. In this context, while the com-

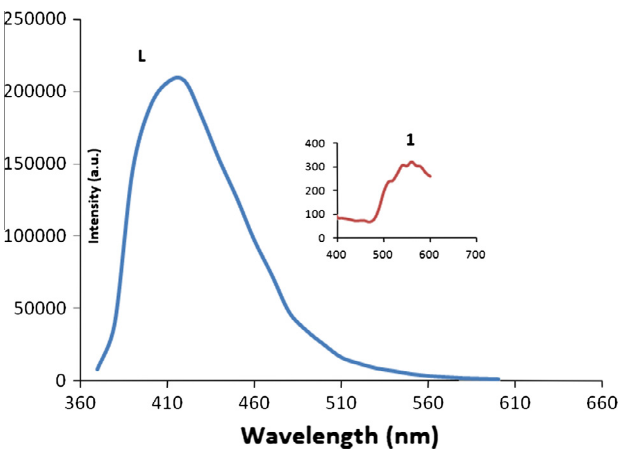


Fig. 7. Fluorescence spectra of **L** and of the complex **1** recorded with an excitation wavelength of 350 nm.

plexes **2** and **3** show no emission, the complex **1** emits at 560 nm with low intensity. Fluorescence of the **L** attributed to the intra-ligand $\pi \rightarrow \pi^*$ transitions at the excited state. However the origin of the luminescence of the complex **1** seems to be more complicated. Because *d*–*d* transitions do not occur in d^{10} complexes, the properties of these systems originate from the other types of electronic transitions. The Cu$\cdots$Cu contacts of 2.570(2) Å are shorter than the sum of the van der Waals radii of two Cu atoms (2.80 Å), which probably allows the contribution from excited states. Thus the poor yellow green emission from complex **1** can be attributed to the metal-to-metal charge transfer (MMCT), to a triplet halide-to-ligand charge-transfer (^{3}XLCT) excited state in the $[Cu_2I_2]$ cores and intra-ligand transitions at the excited state or combinations of these transitions [7].

Conclusion

A new thiophene-substituted benzimidazol ligand, (1-methyl-2-(thiophen-2-yl)-1H-benzo[d]imidazole), and its three copper complexes containing chloride, iodine and nitrate anions were synthesized and characterized. The complex **1** comprises discrete centrosymmetric binuclear $[Cu_2I_2]$ units bridged by two iodine ligands. N-methyl groups and benzimidazole C atoms are involved as donors in weak C—H$\cdots$I hydrogen bonds to create a 3D-network. **2** is a mononuclear copper(II) complex containing two **L** molecules and two chlorine ligands. The complex molecules interact through bifurcated weak C—H$\cdots$Cl hydrogen bonds involving thienyl ring/methyl group C atoms as donors. The crystal structure of the complex **3** contains two symmetry-independent centrosymmetric complex molecules and displaying differences in the nitrate ligands coordination modes which might be attributed to a dynamic Jahn–Teller effect. Solid state fluorescence spectrum of the ligand **L** shows that it is a good candidate for a fluorescent material. On the other hand, complex **1** shows poor yellow–green emission.

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Appendix A. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic data center, and CCDC Nos. 1021305–1021307 for compounds **1**, **2**, and **3**. Copies of this information may be obtained free of charge from the +44(1223)336 033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.10.043.

References

[1] N. Armaroli, G. Accorsi, F. Cardinali, A. Listorti, Top. Curr. Chem. 280 (2007) 69–115.

[2] J.Y. Lu, Coord. Chem. Rev. 246 (2003) 327.

[3] C. Santini, M. Pellei, V. Gandin, M. Porchia, F. Tisato, C. Marzano, Chem. Rev. 114 (2014) 815–862.

[4] CP. Landee, MM. Turnbull, Eur. J. Inorg. Chem. (2013) 2266–2285.

[5] K.A. Wills, H.J. Mandujano-Ramírez, G. Merino, D. Mattia, T. Hewat, N. Robertson, G. Oskam, M.D. Jones, S.E. Lewis, P.J. Cameron, RSC Adv. 3 (2013) 23361–23369.

[6] S.L. Li, X.M. Zhang, Inorg. Chem. 53 (2014) 8376–8383.

[7] P.C. Ford, E. Cariati, J. Bourassa, Chem. Rev. 99 (1999) 3625–3647.

[8] K. Tsuge, Chem. Lett. 42 (2013) 204–208.

[9] T. Wu, D. Li, S.W. Ng, CrystEngComm 7 (2005) 514–518.

[10] N. Kitada, T. Ishida, CrystEngComm 16 (2014) 8035–8040.

[11] L. Gao, J.Y. Wu, M.Y. Li, L. Zhang, P. Zhang, Q.F. Wu, X.Q. Cai, F.T. Chen, S.S. Zhang, Chinese J. Struct. Chem. 32 (2013) 885–889.

[12] Y. Fu, H. Lu, J. Mol. Struct. 892 (2008) 205–209.

[13] R. Peng, M. Li, D. Li, Coord. Chem. Rev. 254 (2010) 1–18.

[14] A. Barbieri, G. Accorsi, N. Armaroli, Chem. Commun. 19 (2008) 2185–2193.

[15] H. Wang, M.X. Li, M. Shao, Z.X. Wang, J. Mol. Struct. 889 (2008) 154–159.

[16] S.E. Castillo-Blum, N. Barba-Behrens, Coord. Chem. Rev. 196 (2003) 3–30.

[17] M. Rozencweig, D.D. Von Hoff, M. Slavik, F.M. Muggia, Ann. Intern. Med. 86 (1977) 803–812.

[18] E.R. Jamieson, S.J. Lippard, Chem. Rev. 99 (1999) 2467–2498.

[19] Ö. Algül, B. Özçelik, U. Abbasoğlu, F. Gümüş, Turk. J. Chem. 29 (2005) 607–615.

[20] K.K. Monthilal, C. Karunakaran, A. Rajendran, R. Murugesan, J. Inorg. Biochem. 98 (2004) 322–332.

[21] M. Devereux, D. O'Shea, M. O'Connor, H. Grehan, G. Connor, M. McCann, G. Rosair, F. Lyng, A. Kellett, M. Walsh, D. Egan, B. Thati, Polyhedron 26 (2007) 4073–4084.

[22] N.M. Aghatabay, A. Neshat, T. Karabiyik, M. Somer, D. Haciu, B. Dülger, Eur. J. Med. Chem. 42 (2007) 205–213.

[23] L. Li, L. Fan, L. Wei, Y. Li, H. Hou, Z. Anorg. Allg. Chem. 640 (2014) 1449–1454.

[24] B. Eren, Y. Bekdemir, Quim. Nova 37 (2014) 643–647.

[25] Stoe & Cie, X-AREA (Version 1.54) and X-RED32 (Version 1.54), Stoe & Cie, Darmstadt, Germany 2002.

[26] G.M. Sheldrick, SHELXTL 5.1, Bruker AXS Inc., 6300 Enterprise Lane, Madison, WI 53719–1173, USA, 1997.

[27] N. Özdemir, B. Eren, M. Dinçer, Y. Bekdemir, Int. J. Quantum Chem. 111 (2011) 3112–3124.

[28] A. Öztekin, B. Özçelik, U. Abbasoğlu, F. Gümüş, Turk. J. Chem. 29 (2005) 607–615.

[29] F. Saczewski, E. Dziemidowicz-Borys, P.J. Bednarski, R. Grünert, M. Gdaniec, P. Tabin, J. Inorg. Biochem. 100 (2006) 1389–1398.

[30] P.N. Preston, The Chemistry of Heterocyclic Compounds: Benzimidazoles and Cogeneric Tricyclic Compounds, John Wiley & Sons. Inc., New York, 2009.

[31] K. Pasterny, R. Wrzalika, T. Kupkaa, G. Pasternaa, J. Mol. Struct. 614 (2002) 297–304.

[32] B. Machura, A. Switlicka, M. Wolff, J. Kusz, R. Kruszynski, Polyhedron 28 (2009) 1348–1354.

[33] K. Kurdziel, T. Głowiak, J. Jezierska, Polyhedron 20 (2001) 3307–3313.

[34] K. Kurdziel, T. Głowiak, Trans. Met. Chem. 24 (1999) 366.

[35] K. Kurdziel, T. Głowiak, J. Jezierska, J. Chem. Soc. Dalton Trans. (2000) 1095–1100.

[36] Cambridge Structural Database (CSD), ver. 5.34, update from May 2013.

[37] A. Toth, C. Floriani, A. Chiesi-Villa, C. Guastini, J. Chem. Soc. Dalton Trans. (1988) 1599–1605.

[38] H. Oshio, T. Watanabe, A. Ohto, T. Ito, H. Masuda, Inorg. Chem. 35 (1996) 472–479.

[39] A. Toth, C. Floriani, A. Chiesi-Villa, C. Guastini, Inorg. Chem. 26 (1987) 3897–3902.

[40] F.F. Belicchi, G.F. Gasparri, C. Pelizzi, P. Tarasconi, Trans. Met. Chem. 10 (1985) 295–299.

[41] G.R. Desiraju, T. Steiner, The Weak Hydrogen Bond in Structural Chemistry and Biology, Oxford University Press, New York, 1999.