Synthesis, characterization and non-linear optical properties of two mononuclear Cu(II) complexes of 2,6-bis(1-butylbenzimidazol-2-yl)pyridine

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1. Introduction

Synthesis of benzimidazole derivatives has received attention due to their remarkable biological activities and clinical applications [1, 2]. Benzimidazole is a heterocyclic organic compound containing a benzene ring fused to an imidazole ring [3]. Benzimidazole compounds exhibit a wide range of biological activities, such as antiviral, antibacterial, antifungal, and antimalarial [4-7].

Biological activity can be predicted by global and local electronic reactivity descriptors calculated with quantum chemical methods. Global chemical reactivity descriptors such as frontier molecular orbital energies ε_HOMO and ε_LUMO, energy gap Δε = ε_LUMO−ε_HOMO, electronegativity χ = −1/2(ε_LUMO+ε_HOMO),

ABSTRACT

Two copper(II) complexes, [Cu(L)(N₃)₂]·MeOH and [Cu(L)(NCS)₂]·MeOH, were prepared and characterized by spectroscopic, analytical, and quantum chemical studies, where L is 2,6-bis(1-butylbenzimidazol-2-yl)pyridine. X-ray quality crystals of [Cu(L)(N₃)₂]·MeOH were obtained by slow evaporation of MeOH solution of the complex. Molecular structure of [Cu(L)(N₃)₂]·MeOH was determined by X-ray crystallography. The asymmetric unit contains one [Cu(L)(N₃)₂] and one MeOH molecule. Cu(II) in [Cu(L)(N₃)₂]·MeOH is five-coordinate, bonded to five nitrogens (three from L and two from two azide anions). Coordination geometry around Cu(II) center is distorted square-pyramidal with τ value of 0.065. Optimized geometries, IR spectra, and non-linear optical properties of the complexes were obtained by computational studies based on density functional theory (DFT) with M062X method. NLO properties of these complexes were investigated computationally and both complexes exhibit better NLO properties than urea.

ARTICLE HISTORY
Received 12 June 2015
Accepted 11 November 2015

KEYWORDS
Cu(II) Complex; benzimidazole; molecular structure; square-pyramidal; non-linear optical properties

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Supplemental data for this article can be accessed at http://dx.doi.org/10.1080/00958972.2015.1134789.
chemical potential $\mu = 1/2(\varepsilon_{\text{LUMO}} + \varepsilon_{\text{HOMO}})$, global hardness $\eta = 1/2(\varepsilon_{\text{LUMO}} - \varepsilon_{\text{HOMO}})$, global softness $S = 1/2\eta$, and electrophilicity index $\omega = \mu^2/2\eta$ are successful in predicting global reactivity trends [8]. Selectivity in a chemical system can be determined by local reactivity descriptors such as Fukui functions, local softness, and local electrophilicity indices. Polarizability and hyperpolarizability are other important parameters for detecting the strength of molecular interactions and non-linear optical (NLO) properties of chemical species. Directly measuring the polarizability and hyperpolarizability of a chemical compound is difficult. Computational studies provide a way to estimate these parameters.

Benzimidazoles are usually prepared by condensation of o-phenylenediamine with carboxaldehydes, carboxylic acids, or their derivatives [9]. N-Substituted benzimidazole derivatives are synthesized by reaction with alkyl/aryl halide in the presence of a base. Several benzimidazole derivatives were synthesized by derivatization at the N–H group [10–12]. In addition to biological importance of benzimidazole derivatives, they form stable complexes with various transition metals [13]. Transition metal complexes containing benzimidazole ligands were synthesized and their properties were extensively investigated by other research groups [14–19].

Recently, we reported the structural and biological properties of Mn(II) and Cu(II) complexes of 2,6-bis(1-butylbenzimidazol-2-yl)pyridine (L) (scheme 1) [20–22]. In continuation of our work on benzimidazole derivatives and their transition metal complexes, we report the synthesis, characterization, and non-linear optical properties of two mononuclear Cu(II) complexes. Additionally, photoluminescence and thermal properties of the complexes were investigated.

2. Experimental

2.1. General methods

All starting materials and organic solvents were purchased from commercial sources and used as-received, unless noted otherwise. IR spectra were performed using KBr pellets on a Perkin Elmer Paragon 1000PC. CHN analysis was performed using a CE-440 Elemental analyzer. $^1$H and $^{13}$C NMR spectra were obtained using a Bruker Avance 400. ESI mass spectra were recorded on a Thermo Fisher Exactive + TriVersa Nanomate mass spectrometer. The electronic spectra from 200 to 900 nm were obtained on a Shimadzu UV-1800 UV–vis spectrophotometer. The single-photon fluorescence spectra were collected on a Perkin Elmer LS55 luminescence spectrometer. Thermal analyses of the complexes were performed on a Perkin Elmer Pyris Diamond.

2.2. X-ray structure solution and refinement for $[\text{Cu}(L)(\text{N}_3)_2]\cdot\text{MeOH}$

Single crystal of dimensions $0.61 \times 0.51 \times 0.10$ mm$^3$ was chosen for the diffraction experiment. Data collection and cell refinement for X-ray crystallography were completed using a Bruker APEX2 CCD diffractometer and data reduction was performed using Bruker SAINT. SHELXTL was used to solve and refine the structures [23]. Diffraction data were measured at 150(2) K using Mo-$K\alpha$ radiation with a

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Scheme 1. 2,6-Bis(1-butylbenzimidazole)pyridine and its Cu(II) complexes.
Bruker ApexII diffractometer [23]. The structure was solved by direct methods and refined on \( F^2 \) using all reflections with SHELXTL [24]. All non-hydrogen atoms were refined using anisotropic atomic displacement parameters. Hydrogens bonded to carbon were inserted at calculated positions and refined using a riding model. Hydrogen of OH was located in a difference map and its positional parameters were freely refined. Details of the crystal data and refinement are given in table 1. Selected bond lengths and angles for the complex are presented in table 2. Refinement of \([\text{Cu}(L)(\text{N}_2)]\cdot\text{MeOH}\) showed a disorder of both butyl chains. First, C1–C4 was modeled over two positions with 75 : 25 (C1–C4 : C1′–C4′) site-occupancy ratio. Second, C25–C27 was modeled over two positions with 70 : 30 (C25–C27 : C25′–C27′) site-occupancy ratio.

### 2.3. Synthesis of 2,6-bis(benzimidazol-2-yl)pyridine and 2,6-bis(1-butylbenzimidazol-2-yl)pyridine (L)

2,6-Bis(benzimidazol-2-yl)pyridine and 2,6-bis(1-butylbenzimidazol-2-yl)pyridine (L) were synthesized by the literature method and characterization data are given in the supplementary file [20–22, 25].

### Table 1. Crystallographic data.

| Complex      | \([\text{Cu}(L)(\text{N}_2)]\cdot\text{MeOH}\) |
|--------------|---------------------------------|
| Empirical formula | \(\text{C}_{28}\text{H}_{33}\text{CuN}_{11}\text{O}\) |
| Formula weight | 603.19 |
| Crystal system | Monoclinic |
| Space group | \(\text{P}2(1)/\text{c}\) |
| Unit cell | |
| \(a (\text{Å})\) | 14.7854(11) |
| \(b (\text{Å})\) | 11.5518(8) |
| \(c (\text{Å})\) | 16.3899(12) |
| \(\alpha^\circ\) | 90 |
| \(\beta^\circ\) | 90.9670(10) |
| \(\gamma^\circ\) | 90 |
| Volume (\(\text{Å}^3\)) | 2799.0(4) |
| \(Z\) | 4 |
| Abs. coeff. (mm\(^{-1}\)) | 0.825 |
| Refl. collected | 27,999 |
| Ind. Refl. \([R_{int}]\) | 6957 [0.0297] |
| \(R_1, wR_2 [I>2\sigma(I)]\) | 0.0302, 0.0770 |
| \(R_1, wR_2 \) (all data) | 0.0399, 0.0822 |
| CCDC | 1,014,561 |

### Table 2. Selected bond lengths [Å] and angles [°] for \([\text{Cu}(L)(\text{N}_2)]\cdot\text{MeOH}\) and \([\text{Cu}(L)(\text{NCS})_2]\).

|          | \([\text{Cu}(L)(\text{N}_2)]\) | \([\text{Cu}(L)(\text{NCS})_2]\) |
|----------|-------------------|-------------------|
| Cu(1)–N(6) | 1.94511 | 1.9589(13) | 1.93874 |
| Cu(1)–N(3) | 2.09064 | 2.0092(12) | 2.08131 |
| Cu(1)–N(4) | 2.11326 | 2.0166(13) | 2.07913 |
| Cu(1)–N(2) | 2.16856 | 2.0270(13) | 2.07823 |
| Cu(1)–N(9) | 2.16818 | 2.1754(14) | 2.20858 |
| N(6)–Cu(1)–N(3) | 166.22152 | 152.35(6) | 163.21136 |
| N(6)–Cu(1)–N(4) | 98.41276 | 97.27(5) | 101.13549 |
| N(3)–Cu(1)–N(4) | 75.74021 | 78.39(5) | 76.84623 |
| N(6)–Cu(1)–N(2) | 105.08707 | 101.36(5) | 101.13804 |
| N(3)–Cu(1)–N(2) | 75.17273 | 78.26(5) | 76.81484 |
| N(4)–Cu(1)–N(2) | 144.36343 | 156.24(5) | 151.79220 |
| N(6)–Cu(1)–N(9) | 107.16001 | 104.13(6) | 113.15274 |
| N(3)–Cu(1)–N(9) | 86.48821 | 103.37(5) | 83.63550 |
| N(4)–Cu(1)–N(9) | 104.55942 | 93.14(5) | 93.06165 |
| N(2)–Cu(1)–N(9) | 93.75565 | 96.45(5) | 93.89338 |
2.4. Synthesis of \([\text{Cu}(L)(N_3)_2]\cdot\text{MeOH} \) and \([\text{Cu}(L)(\text{NCS})_2]\cdot\text{MeOH}\)

To a refluxing solution of \(L\) (0.42 g, 1 mmol) in MeOH (20 mL), Cu(OAc)_2·H_2O (0.20 g, 1 mmol) in MeOH (5 mL) was added, resulting in a green clear solution followed by addition of NaN_3 (0.13 g, 2 mmol) or NaNCN (0.16 g, 2 mmol). Resulting solution was refluxed for 2 h and then allowed to cool to room temperature. Green precipitates were collected and washed with cold MeOH (5 mL) and diethyl ether (10 mL).

2.4.1. \([\text{Cu}(L)(N_3)_2]\cdot\text{MeOH}\)

**Yield:** 0.45 g, 75% (based on Cu^{2+}) **Color:** Green. m.p decompose 325 °C. **Elemental analysis data:** Anal. (%) calculated for C_{27}H_{29}N_5Cu(N_3)_2·CH_3OH (603.18): C, 55.75; H, 5.51; N, 25.54. Found (%): C, 55.62; H, 5.27; N, 25.09. **IR (KBr, \(\nu\), cm\(^{-1}\))**: 2961, 2930, 2871, 2042, 1590, 1568, 1509, 1478, 1436, 1328, 1196, 1158, 1087, 925, 745, 672, 465, 431 cm\(^{-1}\). **Mass spect (eSI):** m/z 1100.37(15%) \([\text{Cu}(L)(N_3)_2]^{2+}\), 528.18(45%) \([\text{Cu}(L)(N_3)]^+\), 486.17(100%) \([\text{Cu}(L)]^+\). **\(\Lambda_m\)**: 5.20 Ω\(^{-1}\)cm\(^2\) mol\(^{-1}\).

2.4.2. \([\text{Cu}(L)(\text{NCS})_2]\cdot\text{MeOH}\)

**Yield:** 0.52 g, 82% (based on Cu^{2+}) **Color:** Green. m.p decompose 330 °C (decomp.). **Elemental analysis data:** Anal. (%) calculated for C_{27}H_{29}N_5Cu(NCS)_2 (603.26): C, 57.74; H, 4.85; N, 16.25. Found (%): C, 57.54; H, 4.65; N, 16.16. **IR (KBr, \(\nu\), cm\(^{-1}\))**: 2958, 2930, 2871, 2074, 1585, 1573, 1514, 1483, 1442, 1334, 1199, 1157, 1088, 925, 744, 672, 467, 425 cm\(^{-1}\). **Mass spect (EISI):** m/z 1635.34(5%) \([\text{Cu}(L)(\text{NCS})_3]^3+\), 1148.26(5%), \([\text{Cu}(L)(\text{NCS})_2](\text{NCS})^+\), 544.14(100%) \([\text{Cu}(L)(\text{NCS})]^+\), 486.17(70%) \([\text{Cu}(L)]^+\). **\(\Lambda_m\)**: 6.10 Ω\(^{-1}\)cm\(^2\) mol\(^{-1}\).

2.5. Computational method

Electronic structure of \([\text{Cu}(L)(N_3)_2]\) and \([\text{Cu}(L)(\text{NCS})_2]\) was pictured with Gauss view 5.0.8 program [26]. Optimizations of all electronic structures were performed with Gaussian 09 AMD64 D.0.1 version [27]. M062X method of density functional theory was used at geometry optimizations. Geometry optimizations were followed with frequency calculations. No imaginary frequencies were obtained for optimized structures. LANL2DZ basis set for copper and 6-31G+(d) basis set for the other atoms were used in calculations using GEN key word.

3. Results and discussion

The benzimidazole ligand 2,6-bis(1-butylbenzimidazol-2-yl)pyridine (L) was prepared according to the literature method [22]. Spectroscopic data for the ligand are given in the supplementary file. The purity of the ligand was checked by elemental analysis, \(^1H–^1{}^3C\) NMR and ESI mass spectra. Both \(^1H\) and \(^1{}^3C\) NMR spectra of the ligand are in agreement with the previous studies [22]. The Cu(II) complexes of the ligand with two different coordinating anions (Cl\(^-\) and NO\(^3\)\(^-\)) were synthesized by our groups [21]. In this study, the Cu(II) complexes \([\text{Cu}(L)(N_3)_2]\cdot\text{MeOH} \) and \([\text{Cu}(L)(\text{NCS})_2]\cdot\text{MeOH}\) of the ligand (L) with two different coordinating anions (NCS\(^-\) and N\(_3\)\(^-\)) were obtained and characterized by spectroscopic and analytical methods. The potential application of these complexes in non-linear optic materials was investigated using computational methods.

\([\text{Cu}(L)(N_3)_2]\cdot\text{MeOH} \) and \([\text{Cu}(L)(\text{NCS})_2]\cdot\text{MeOH}\) are soluble in MeOH, EtOH, DMF, and DMSO and not soluble in water and diethyl ether. The elemental analysis data are in agreement with calculated values. IR spectra of the complexes are similar except for anion vibrations; the bands observed at 2960–2870 cm\(^{-1}\) can be attributed to aliphatic \(\nu(C–H)\). The \(\nu(C=\text{N})\) vibrations shifted to lower values (red shift) for the complexes showing involvement of the benzimidazole nitrogens (C=\(\text{N}\)) in coordination with Cu(II) [28, 29]. The \(\nu(C=\text{N})\) vibrations for \([\text{Cu}(L)(N_3)_2]\cdot\text{MeOH} \) and \([\text{Cu}(L)(\text{NCS})_2]\cdot\text{MeOH}\) were observed at 1590 and 1585 cm\(^{-1}\), respectively. In IR spectra of \([\text{Cu}(L)(N_3)_2]\cdot\text{MeOH}, \) the strong azide stretch was observed at 2042 cm\(^{-1}\). The strong band at 2074 cm\(^{-1}\) was assigned to thiocyanate stretch for \([\text{Cu}(L)(\text{NCS})_2]\cdot\text{MeOH}\).

The ESI spectra of the complexes were investigated in MeOH. In ESI mass spectra of the complexes, signals due to single-charged ions were observed for both complexes. In mass spectra of \([\text{Cu}(L)(N_3)_2]\cdot\text{MeOH} \) and \([\text{Cu}(L)(\text{NCS})_2]\cdot\text{MeOH}\) are soluble in MeOH, EtOH, DMF, and DMSO and not soluble in water and diethyl ether. The elemental analysis data are in agreement with calculated values. IR spectra of the complexes are similar except for anion vibrations; the bands observed at 2960–2870 cm\(^{-1}\) can be attributed to aliphatic \(\nu(C–H)\). The \(\nu(C=\text{N})\) vibrations shifted to lower values (red shift) for the complexes showing involvement of the benzimidazole nitrogens (C=\(\text{N}\)) in coordination with Cu(II) [28, 29]. The \(\nu(C=\text{N})\) vibrations for \([\text{Cu}(L)(N_3)_2]\cdot\text{MeOH} \) and \([\text{Cu}(L)(\text{NCS})_2]\cdot\text{MeOH}\) were observed at 1590 and 1585 cm\(^{-1}\), respectively. In IR spectra of \([\text{Cu}(L)(N_3)_2]\cdot\text{MeOH}, \) the strong azide stretch was observed at 2042 cm\(^{-1}\). The strong band at 2074 cm\(^{-1}\) was assigned to thiocyanate stretch for \([\text{Cu}(L)(\text{NCS})_2]\cdot\text{MeOH}\).

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(NCS)$_2$]-MeOH (figure 1), the signals at m/z 544.14 (100%) and 486.17 (70%) were assigned to the singly charged complex cations Cu(L)(NCS)$^+$ and [Cu(L)]$^+$, respectively. A higher signal with lower intensity at m/z 1148.26 (5%) was assigned to [Cu(L)(NCS)$_2$](NCS)$^+$. Mass spectrum of [Cu(L)(N$_3$)$_2$]-MeOH showed signals at 528.18 (45%) and 486.17 (100%) assigned to [Cu(L)(N$_3$)]$^+$ and [Cu(L)]$^+$, respectively.

Molar conductance of [Cu(L)(N$_3$)$_2$]-MeOH and [Cu(L)(NCS)$_2$]-MeOH in MeOH (10$^{-3}$ M) is 5.20 and 6.10 Ω$^{-1}$cm$^2$ mol$^{-1}$, respectively, indicating the non-electrolyte nature of the complexes in MeOH solution. The conductance shows that azide and thiocyanate ions are present in the coordination sphere in MeOH solution.

The UV–vis absorption spectra of the complexes were investigated from 200 to 800 nm in MeOH (10$^{-5}$ M). The UV–vis spectra of both complexes show three absorption bands. Bands at 400–348 nm can be attributed to n–π* transitions of the ligand. The bands at 350–270 nm can be assigned to π–π* transitions of aromatic rings. The band at 405–425 nm was assigned to M → L charge transfer transition. No d–d transitions were observed for either complex at the concentration studied.

Thermal studies of the Cu(II) complexes were performed under nitrogen from 20 to 800 °C. Thermal curves for the complexes are shown in figure S1. Thermal decomposition of [Cu(L)(N$_3$)$_2$]-MeOH starts at 250 °C. The complex has three decomposition steps; in the first step, about 5% of the mass was lost from 250 to 300 °C. This loss may be attributed to hydrogen-bonded methanol in the complex. In the second step, approximately, 50% of the sample was removed from the structure at 250–300 °C. The rest of the organic moiety decomposes gradually at high temperature leaving metal oxide as a final residue (CuO). [Cu(L)(NCS)$_2$]-MeOH was thermally stable up to 330 °C. Approximately, 55% of the mass was lost from 330 to 400 °C; the rest decomposes at high temperature leaving metal oxide.

3.1. Molecular structure of [Cu(L)(N$_3$)$_2$]-MeOH

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of MeOH solution of the complex. Molecular structure of the complex is shown in figure 2. The asymmetric unit contains one [Cu(L)(N$_3$)$_2$] and one MeOH. The MeOH binds via O1–H⋯N9 hydrogen bonding to the azide nitrogen (table 3).

Figure 1. ESI mass spectrum of [Cu(L)(NCS)$_2$]-MeOH.
A geometry parameter $\tau$, defined as $\tau = (\beta - \alpha)/60$ where $\beta$ and $\alpha$ are the two largest angles ($\beta > \alpha$), provides a measure of the degree of square-pyramidal (SP) versus trigonal bipyramidal (TBP) geometry. For an ideal square-pyramid, $\tau$ is zero, and for an ideal trigonal bipyramid, $\tau$ becomes 1.0 [30]. In [Cu(L)(N₃)₂]·MeOH, the largest angles within the four N-Cu-N angles are $\alpha = 152.35(6)°$ and $\beta = 156.24(5)°$. Thus, $\tau$ is $(156.24 - 152.35)/60 = 0.065$. This indicates that the geometry around Cu(II) is slightly distorted SP. Four nitrogens (N2, N3, N4 and N6) are located at the basal plane and N9 of an azide is located at the apical position. Cu1–N9 (apical position) distance of 2.1754(14) Å is longer than Cu1–N distances at the basal plane (table 2). Short intermolecular contacts (C9⋯C16 3.375 Å; N6⋯C11 3.110 Å) point to π–π and π–N interactions between inversion-related molecules (figure 3). Crystal packing of the complex is shown in figure 4.

Comparison of the reported crystal structure with the structures of two Cu(II) complexes formed with the same benzimidazole ligand, formulas of the complexes here, determined by our group earlier [20, 21], reveals that in all complexes, the Cu(II) ion adopts a distorted square-pyramidal geometry with similar Cu–N distances.

3.2. Optimized structures

The complexes are optimized at M062X/6-31 + G(d)(LANL2DZ) levels in the gas phase and presented in figure 5. Structural parameters are given in table 2. Experimental and computational structural parameters are subjected to correlation analysis and a graph is plotted to calculate correlation constant ($R^2$). This graph is presented in figure 6. This correlation constant shows that there is a good agreement between experimental and calculated structural parameters. $\tau$ values are re-calculated as 0.36 and 0.19 for [Cu(L)(N₃)₂] and [Cu(L)(NCS)₂], respectively. According to these values, geometry is distorted SP for each complex. IR spectra of the complexes are calculated at the same level of theory. Some selected harmonic vibrational frequencies are given in table 4. According to table 4, there are some differences between experimental and calculated frequencies, but these are in acceptable limits.
3.3. Non-linear optical (NLO) properties

NLO properties provide the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory. Therefore, the NLO properties play a significant role for design of...
The NLO properties increase with conjugation of π electrons or adding donor/acceptor groups to molecules. Total static dipole moment (μ), the average linear polarizability (α), the anisotropy of polarizability (Δα), and first hyperpolarizability (β) can be used to describe the relationship between the electronic structures of molecules and their NLO properties. The average linear polarizability, the anisotropy of polarizability, and first hyperpolarizability increase with increasing the delocalization of π electrons. Therefore, the NLO properties increase with increasing these parameters. Urea is selected as a reference substance and these parameters of urea are calculated with 6–31 + G(d) basis set using equations (1)–(4) \cite{31, 32} and given in table 5.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

(1)
All values of the complexes are greater than urea values. Therefore, NLO properties of the complexes are better than urea. The general ranking of NLO properties should be as follows:

$[\text{Cu(L)(N)}_3\text{S}_2]\text{MeOH} > [\text{Cu(L)(NCS)}_2] > \text{Urea}$

As can be seen from the above rankings, $[\text{Cu(L)(NCS)}_2]$ is the best candidate for NLO applications.

### 3.4. Photoluminescence properties of the Cu(II) complexes

The single-photon fluorescence spectra of the metal complexes were collected on a Perkin Elmer LS55 luminescence spectrometer. All samples were prepared in spectrophotometric grade solvents and analyzed in a 1-cm optical path quartz cuvette. Solutions of the ligand were prepared at $(1 \times 10^{-3} - 1 \times 10^{-7} \text{ mol L}^{-1})$ concentrations. The emission and excitation spectra of the metal complexes in ethanol are shown in figure 7 and the obtained data are given in table 6. In excitation spectra of the $[\text{Cu(L)}(\text{N})_3\text{S}_2] \cdot \text{MeOH}$ complex in ethanol, one excitation band was observed from 355 to 375 nm with...
Upon excitation at 355–375 nm, the complex shows only one emission band at 490–510 nm in ethanol. Upon dilution, the excitation bands shift to shorter wavelengths, however, the emission bands shifted to longer wavelength values in ethanol. \([\text{Cu(L)(NCS)}_2]\)·MeOH shows very similar photoluminescence properties to the azide analog. \([\text{Cu(L)(NCS)}_2]\)·MeOH exhibits one emission band at 502–520 upon excitation at 370–383 nm in ethanol.

4. Conclusion

Two copper(II) complexes of a benzimidazole ligand, 2,6-bis(1-butylbenzimidazol-2-yl)pyridine, were prepared and characterized by spectroscopic and analytical methods. Molecular structure of \([\text{Cu(L)(N}_3])_2\)·MeOH was determined by single-crystal X-ray diffraction. Cu(II) in \([\text{Cu(L)(N}_3])_2\)·MeOH is five-coordinate, bonded to five nitrogens. Coordination geometry around Cu(II) is distorted square-pyramidal with a \(\tau\) value of 0.065. The complexes are optimized using M062X method with LANL2DZ and 6–31 + G(d) basis set.
basis sets in the gas phase. NLO properties of these complexes were investigated computationally and both complexes exhibit better NLO properties than urea.

**Supplementary material**

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center; CSD reference for [Cu(L)(N$_2$)$_2$]·MeOH is 1014561. Copies of this information can be obtained from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax:+44 1223 335033; E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

**Disclosure statement**

No potential conflict of interest was reported by the authors.

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