

# Binuclear Nickel(II) Complex Containing 6-Methyl-2,2'-bipyridine and Chloride Ligands: Synthesis, Characterization, Thermal Analyses, and Crystal Structure Determination

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**ABSTRACT:** A new binuclear complex of  $[\{NiCl(6-mbipy)\}_2(\mu-Cl)_2]$  (**I**) was prepared from the reaction of  $NiCl_2 \cdot 6H_2O$  and 6-methyl-2,2'-bipyridine (6-mbipy) in a mixture of methanol and acetonitrile. Suitable crystals of **I** for X-ray diffraction measurement were obtained by slow evaporation of the resulted green solution at room temperature. Complex **I** was characterized by spectral methods (IR, UV-Vis, and luminescence), elemental analysis (CHN), and single-crystal X-ray diffraction. The structure of **I** is centrosymmetric binuclear complex and each Ni(II) cation is five-coordinated in a slightly distorted square-pyramidal configuration. In this binuclear complex, the Ni...Ni distance is 3.533(1) Å. Furthermore, the luminescence emission of the title complex was blue-shifted and is stronger than that of free 6-methyl-2,2'-bipyridine ligand. Thermal stabilities of this complex was also studied by thermogravimetric analysis.

**KEYWORDS:** Crystal structure; Nickel(II) complex; 6-Methyl-2,2'-bipyridine; Luminescence spectroscopy; Thermogravimetric analysis.

## INTRODUCTION

In recent years, nickel(II) complexes including N,N'-chelating ligands have been rapidly developed due to their potential applications as catalysts for ethylene polymerization [1-3], as antimicrobial [4], anticancer and cytotoxic agents [5-7], and special magnetic [8, 9] and luminescence properties [10-12]. In this regards, 6-methyl-2,2'-bipyridine is a good bidentate ligand that can be coordinated to the different metals in their various

oxidation states. This ligand was first synthesized by Haginiwa *et al.*; in 1975, from the reaction of 2-methylpyridine with pyridine-N-oxide in the presence of platinumed palladium-carbon catalyst [13]. To the best of our knowledge there are some reports on the coordination compounds containing this ligand, such as  $[Pt(6-mbipy)Cl_4]$ , [14],  $[Cu(6-mbipy)_2](PF_6)_2$ , [15],  $[Ti(6-mbipy)Cl_3(DMSO)]$ , [16],  $[Ru(6-mbipy)_3](BF_4)_3$ , [17],  $[Hg(6-mbipy)(SCN)_2]$ , [18],

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[Zn(6-mbipy)(NO<sub>3</sub>)<sub>2</sub>], [19], [Cd(6-mbipy)(NO<sub>3</sub>)<sub>2</sub>], [20], [Fe<sub>2</sub>(6-mbipy)<sub>2</sub>(NCS)<sub>4</sub>(μ-bipym)<sub>2</sub>] (where bipym is 2,2'-bipyrimidine), [21], [Cu(6-mbipy)<sub>2</sub>(OH-BF<sub>3</sub>)(PF<sub>6</sub>)], [22], [Fe(6-mbipy)<sub>3</sub>(ClO<sub>4</sub>)<sub>2</sub>.6-mbipy], [23], [Mn(6-mbipy)F<sub>3</sub>(H<sub>2</sub>O)], [24], [Pd(6-mbipy)<sub>2</sub>(CF<sub>3</sub>SO<sub>3</sub>)<sub>2</sub>], [25], [Ru(6-mbipy)<sub>3</sub>(BF<sub>4</sub>)<sub>2</sub>], [26], [Zn(6-mbipy)Cl<sub>2</sub>], [27], [Hg(6-mbipy)Cl<sub>2</sub>], [28], [Zn(6-mbipy)Br<sub>2</sub>], [29], [Pb<sub>4</sub>(6-mbipy)<sub>4</sub>(μ-NO<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>], [30], [Co(6-mbipy)Cl<sub>2</sub>], [31], [Cd(6-mbipy)Br<sub>2</sub>(DMSO)], [32], [Au<sub>2</sub>(6-mbipy)<sub>2</sub>(μ-oxo)<sub>2</sub>(PF<sub>6</sub>)<sub>2</sub>.CH<sub>3</sub>CN], [33] and [Pt(6-mbipy)Cl<sub>4</sub>], [34]. These complexes are interest owing to their importance for applications in spectroscopy [14-20], magnetism [21-24], crystallography [25-32] and anticancer and cytotoxic agents [33, 34]. In continuation of these research works, herein, we report the synthesis of a new centrosymmetric binuclear complex of [{NiCl(6-mbipy)}<sub>2</sub>(μ-Cl)<sub>2</sub>] (**1**). The structure of this complex was studied by thermogravimetric analysis, elemental analysis, X-ray crystallography as well as UV-Vis, IR and luminescence spectroscopic techniques. Furthermore, this complex is, to the best of our knowledge, the first structurally characterized example of Ni(II) complex containing 6-methyl-2,2'-bipyridine ligand.

## EXPERIMENTAL SECTION

### Materials and Physical Methods

6-Methyl-2,2'-bipyridine ligand and NiCl<sub>2</sub>.6H<sub>2</sub>O salt were purchased from Aldrich and used as received. All solvents were purchased from Merck and used without further purification. Elemental analyses were performed on an Elementar Analysensystem GmbH VarioEL CHN-O analyzer. Infrared spectrum (4000–500 cm<sup>-1</sup>) was recorded on a Thermo Nicolet NEXUS 870 FT-IR ESP, from 4000-500 cm<sup>-1</sup> in KBr pellet and from 500-50 cm<sup>-1</sup> dispersed on the polyethylene thin-film. Melting point was determined on a Barnstead Electrothermal IA 9100 melting point apparatus. Thermal behavior was measured with Netzsch TG 209F1 instrument. UV-Vis spectra were recorded on a Perkin Elmer Precisely PTP-1 Peltier System using a 1 cm path length cell in methanol at room temperature, and luminescence spectra were recorded on a FP-6200 spectrofluorometer using a 1 cm path length cell in methanol at room temperature.

### Synthesis of [{NiCl(6-mbipy)}<sub>2</sub>(μ-Cl)<sub>2</sub>] (**1**)

6-Methyl-2,2'-bipyridine (0.32 g, 0.29 mL, 1.80 mmol) in 30 mL methanol was added to a solution of NiCl<sub>2</sub>.6H<sub>2</sub>O

(0.44 g, 1.80 mmol) in acetonitrile (10 mL) and the resulting green solution was stirred for 15 min at 40 °C. This solution was left to evaporate slowly at room temperature. After ten days, green block single crystals of **1** suitable for X-ray analyses were obtained (yield 0.41 g, 76.0%, m. p. > 300 °C). Infrared frequencies for free 6-methyl-2,2'-bipyridine ligand and complex **1** are reported in Table 1. UV-Vis: λ<sub>max</sub> (CH<sub>3</sub>OH, nm), for free 6-methyl-2,2'-bipyridine ligand: 206, 236, 285 and for complex **1**: 209, 245, 300, 312. Elemental analysis: C<sub>22</sub>H<sub>20</sub>Cl<sub>4</sub>N<sub>4</sub>Ni<sub>2</sub> (%) (599.60); Anal. Calcd (%): C, 44.07; H, 3.34; N, 9.34. Found: C, 43.84; H, 3.32; N, 9.27.

### Crystal structure determination and refinement

The data collection for **1** was made on a Bruker APEX II CCD area detector diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 298 K. The structure was solved by SHELX-97 and absorption correction was done using the SADABS program [35]. Data collection, cell refinement, and data reduction were performed by applying APEX II, SAINT, SHELXTL and PLATON program packages [35-37]. The molecular graphics were generated by using Mercury 2.4 program [38].

## RESULTS AND DISCUSSION

### Synthesis of **1**

Complex **1** was obtained from the reaction of one equivalent of 6-methyl-2,2'-bipyridine ligand with one equivalent of NiCl<sub>2</sub>.6H<sub>2</sub>O in a mixture of methanol and acetonitrile. Suitable crystals of **1** for X-ray diffraction measurement were obtained by slow evaporation of the resulted green solution at room temperature.

### Spectroscopic characterization of [{NiCl(6-mbipy)}<sub>2</sub>(μ-Cl)<sub>2</sub>] (**1**)

The infrared spectra in Table 1 and figure S1 show the vibration frequencies for free 6-mbipy ligand [18] and complex **1**. The infrared spectra of free 6-mbipy ligand and complex **1** show several weak and medium absorption bands in the region of 3105–2916 cm<sup>-1</sup>, which are assigned to the C-H stretching vibrations of the pyridine rings and methyl groups. In the IR spectra of free 6-mbipy and complex **1**, medium-to-strong vibrational bands in the region of 1599-550 cm<sup>-1</sup> are assigned to the hetero aromatic ring modes related to C=C, C=N and C-C [10,14, 18, 39, 40]. These absorption

Table 1: Infrared frequencies of 6-mbipy and complex 1 (cm<sup>-1</sup>).

Compound	$\nu(\text{C-H})$	$\nu(\text{C=C}), \nu(\text{C=N}), \nu(\text{C-C})$	$\delta(\text{C=C}), \delta(\text{C=N}), \delta(\text{C-C})$	$\nu(\text{Ni-N})$	$\nu(\text{Ni-Cl})$	$\nu(\text{Ni-}\mu\text{Cl})$
6-Mbipy	3059w, 3007w, 2922w	1579s, 1459s, 1428s, 1373w, 1269w, 1251m	1149m, 1085s, 1043m, 992m, 813w, 772s, 742m, 640m, 550m	-	-	-
1	3105m, 3062m, 2916w	1599s, 1568s, 1488m, 1454s, 1380m, 1295m, 1249m	1179m, 1157m, 1099m, 1031s, 1019m, 813m, 779s, 734m, 646m, 594m	294m, 278m	262m	242m

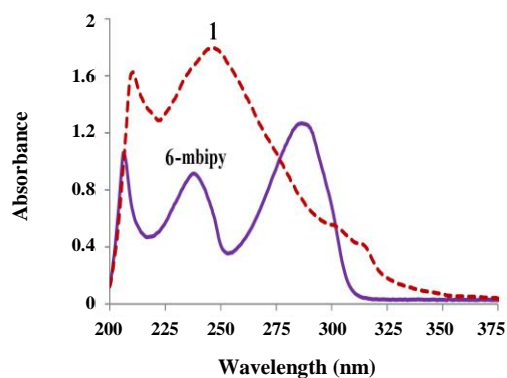


Fig. 1: Absorption spectra of 6-mbipy ( $6 \times 10^{-5} \text{ M}$ ) and 1 ( $7 \times 10^{-5} \text{ M}$ ), in methanol solution.

bands for the free 6-mbipy ligand are shifted to higher frequencies upon coordination in title complex. This shift to higher frequencies upon coordination to metal has been observed for 2,2'-bipyridine ligand and its derivatives coordinated to metals as well, and can be explained by changing the geometry of the free ligands from *anti* to *syn* orientation in the complexes [10,14, 18, 39]. Far infrared spectrum for title complex was observed between 500 and 50 cm<sup>-1</sup>. The Ni-N stretching vibrations were observed at 294 and 278 cm<sup>-1</sup>. Due to the difference between the two Ni-N bond lengths in title complex, as we discussed in the X-ray structure section, two medium Ni-N absorption bands in the IR spectrum of title complex were observed. Furthermore, the medium absorption bands observed at 262 and 242 cm<sup>-1</sup> are assigned to Ni-Cl<sub>terminal</sub> and Ni-Cl<sub>bridge</sub> stretching vibrations, respectively. These assigned absorption bands in the far infrared spectrum of 1 are in the expected ranges and are in accord with similar complexes in the literature [41-43].

Fig. 1 depicts the UV-Vis spectra of the free 6-mbipy ligand and complex 1 in methanol solution. As shown in this figure, the UV-Vis spectra of these compounds have strong absorption bands in the range 206-285 nm, which

can be assigned to the intra ligand  $\pi$ - $\pi^*$  transitions. Also, in the UV-Vis spectrum of 1, there are two medium absorption bands at 300 and 312 nm, which can be assigned to metal-to-ligand charge transfer (MLCT) [44]. Inspection of the UV-Vis spectra shows that the absorbance of title complex is observed as weak shoulder of strong peak around 275 nm.

The luminescence emission spectra for the free 6-mbipy ligand and complex 1 were obtained in methanol solution at room temperature and the results are displayed in Fig. 2. As shown in this figure, the maximum emission spectrum of free 6-mbipy ligand at 306 nm is shifted to 301 nm in the complex. The maximum emission wavelength of complex 1 undergoes a slight (about 5 nm) blue shift, compared with that of free 6-mbipy ligand. Also, the intensity of the luminescent emission band of 1 is stronger than that of the emission band for the free 6-mbipy ligand. The similarity of the shapes of the emission spectra of free 6-mbipy ligand and title complex suggests their identical origins from ligand centered transitions (LC, as  $\pi^* \rightarrow \pi$  or  $\pi^* \rightarrow n$  transitions). The observed blue shift for complex 1 can be explained with a decrease of the energy gap between the ground and excited states in the 6-mbipy ligand upon coordinated to Ni(II) cation [45-49].

#### Thermal studies of $[\{\text{NiCl}(\text{6-mbipy})\}_2(\mu\text{-Cl})_2] (\text{I})$

Thermogravimetric analysis of the complex 1 has been determined on single-crystalline samples between 30 and 780 °C under a nitrogen atmosphere with a heating rate of 10 °C min<sup>-1</sup> and the result is displayed in Fig. 3. The TGA curve for this complex shows a five-step thermal decomposition. The first step between 315 and 355 °C with a mass loss of 5.5% corresponds to the loss of two methylene groups (calcd. 4.7%) and remaining weight corresponds to two [Ni(bipy)Cl<sub>2</sub>] complexes. In the last four steps between 360 and 670 °C the two 2,2'-bipyridine (bipy) ligands and the four chloride anions are lost and the framework decomposes (76.4%, calcd: 75.7%).

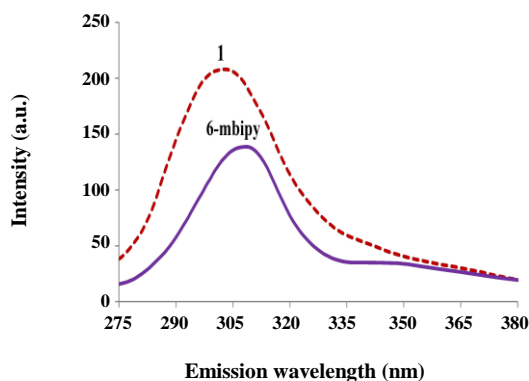


Fig. 2: The luminescence spectra of 6-mbipy ( $3.34 \times 10^{-4}$  M) and 1 ( $3.32 \times 10^{-4}$  M) in methanol solution at room temperature; excitation wavelength = 245 nm.

The final residual weight is 18.1% corresponding to two zero-valent nickel (calcd. 19.6 %) [50].

#### Description of the molecular structure of $[\{\text{NiCl}(6\text{-mbipy})\}_2(\mu\text{-Cl})_2]$ (1)

Crystallographic data for title complex are given in Table 2 and selected bond lengths and angles are presented in Table 3. The coordination polyhedral and molecular structure of the centrosymmetric binuclear  $[\{\text{NiCl}(6\text{-mbipy})\}_2(\mu\text{-Cl})_2]$  (1) complex with the atomic labeling scheme are shown in Figs. 4 and 5, respectively. As shown in these figures, there is a half of  $[\{\text{NiCl}(6\text{-mbipy})\}_2(\mu\text{-Cl})_2]$  molecule in the asymmetric unit and the coordination geometry around nickel(II) cation is five-coordinated in a distorted square-pyramidal configuration ( $\tau = 0.34$ ;  $\tau = (\beta - \alpha)/60$ , where  $\beta = \text{N1-Ni-Cl2} = 172.68^\circ$  and  $\alpha = \text{Cl1-Ni-Cl2}^i = 152.29^\circ$  ( $i = -x+1, -y+2, -z+2$ ), the  $\tau$  parameter being 0 and 1 for perfect square-pyramidal and trigonal-bipyramidal geometries, respectively [51]) by two N atoms from the chelating 6-methyl-2,2'-bipyridine ligand (N1 in equatorial position and N2 in axial position), two bridging chloride anions (Cl2 and Cl2<sup>i</sup> in equatorial positions) and one terminal chloride anion (Cl1 in equatorial position). The two nickel(II) and two bridging chloride constitute a perfect plane, with no deviation from the main plane of Ni<sub>2</sub>Cl<sub>2</sub> moiety. In this plane, the Ni1-Cl2-Ni1<sup>i</sup> angle is  $95.77(5)^\circ$  and the Ni1...Ni1<sup>i</sup> ( $i = -x+1, -y+2, -z+2$ ) distance is  $3.533(1)\text{\AA}$ . The distance between the nickel(II) cation and the bridging chloride anions [ $\text{Ni1}-\mu\text{Cl2} = 2.3795(13)$

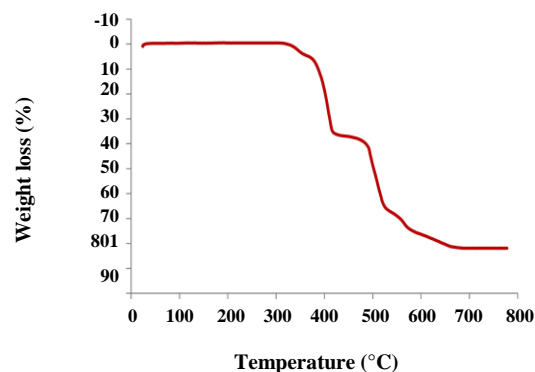


Fig. 3: TGA curve of 1.

and  $\text{Ni1}-\mu\text{Cl2}^i = 2.3831(15)\text{\AA}$ ] is significantly longer than that of the nickel(II) cation and the terminal chloride anion [ $\text{Ni1}-\text{Cl1} = 2.2819(17)$ ]. Furthermore, the equatorial Ni-N distance of  $2.054(4)\text{\AA}$  is slightly longer than the axial Ni-N distance of  $2.002(4)\text{\AA}$ , as anticipated for a square-pyramidal complex. The Ni-N and Ni-Cl bond lengths and angles (Table 3) are in good agreement with the corresponding values in  $[\{\text{NiCl}(\text{L})\}_2(\mu\text{-Cl})_2]$  [52], (L is 2-(pyrid-2-yl)quinoxaline). In this binuclear complex, the Ni1...Ni1<sup>i</sup> distance,  $3.533(1)\text{\AA}$ , is slightly similar to that found in  $[\{\text{NiCl}(\text{L})\}_2(\mu\text{-Cl})_2]$ ,  $3.564(1)\text{\AA}$ , [52] and in  $[\{\text{NiCl}(\text{L})\}_2(\mu\text{-Cl})_2]$ ,  $3.506(2)\text{\AA}$ , [53], (L is 2-(2-furylmethyliminomethyl)pyridine). In addition, in this complex, the pyridine rings are distorted from planarity. The mean planes of rings A(N1/C2-C6), B(N2/C7-C11) and C(Ni1/N1/C6/C7/N2) make the following dihedral angles with each other: A/B =  $9.35^\circ$ , A/C =  $5.00^\circ$  and B/C =  $4.61^\circ$ .

In the crystal structure of the title complex (Fig. 6), there are intermolecular C-H...Cl hydrogen bonds (C4-H4...Cl2<sup>i</sup>, H...A  $2.836\text{\AA}$ , D...A  $3.62(1)\text{\AA}$ , D-H...A  $143^\circ$ ; C5-H5...Cl1<sup>ii</sup>, H...A  $2.822\text{\AA}$ , D...A  $3.60(2)\text{\AA}$ , D-H...A  $139^\circ$ ,  $i = -x, 2-y, 1-z$  and  $ii = x, y, -1+z$ ) and  $\pi\cdots\pi$  interactions between the pyridine rings, Cg3...Cg3<sup>i</sup> and Cg3...Cg3<sup>ii</sup> [distances are  $4.026(5)$  and  $3.721(5)\text{\AA}$ , respectively, symmetry codes:  $i = -x, 2-y, 1-z$  and  $ii = 1-x, 2-y, 1-z$ , and Cg3 is centroid of the ring (N1/C2-C6)]. These intermolecular C-H...Cl hydrogen bonds and  $\pi\cdots\pi$  interactions are effective in the stabilization of the crystal structure and formation of a three-dimensional supramolecular structure.

Table 2: Crystallographic and structure refinement data for 1.

Formula	$C_{22}H_{20}N_4Ni_2$
Formula weight	599.60
Temperature /K	298(2)
Wavelength $\lambda$ /Å	0.71073
Crystal system	Triclinic
Space Group	$P\bar{1}$
Crystal size /mm <sup>3</sup>	0.15×0.12×0.10
$a$ /Å	7.5947(18)
$b$ /Å	8.883(2)
$c$ /Å	10.539(2)
$\alpha$ /°	108.655(18)
$\beta$ /°	105.471(18)
$\gamma$ /°	105.124(19)
Volume / Å <sup>3</sup>	600.8(2)
$Z$	1
Density (calc.) /g cm <sup>-1</sup>	1.657
$\theta$ ranges for data collection	2.62-26.99
F(000)	304
Absorption coefficient mm <sup>-1</sup>	2.030
Index ranges	-9 ≤ h ≤ 9
	-11 ≤ k ≤ 11
	-13 ≤ l ≤ 13
Data collected	5603
Unique data ( $R_{int}$ )	2620, 0.0651
Parameters, restraints	145, 0
Final $R_1$ , $wR_2$ (Obs. data)	0.0523, 0.1441
Final $R_1$ , $wR_2$ (All data)	0.0713, 0.1790
Goodness of fit on $F^2$ (S)	1.099
Largest diff peak and hole /e.Å <sup>-3</sup>	0.829, -0.895

Table 3: Bond distances (Å) and bond angles (°) for 1.

Ni1-N1	2.054(4)	N2-Ni1-Cl2	100.23(14)
Ni1-N2	2.002(4)	N1-Ni1-Cl2	172.68(13)
Ni1-Cl1	2.2819(17)	Cl1-Ni1-Cl2	92.88(6)
Ni1-Cl2	2.3795(13)	N2-Ni1-Cl2 <sup>i</sup>	100.31(13)
Ni1-Cl2 <sup>i</sup>	2.3831(15)	N1-Ni1-Cl2 <sup>i</sup>	88.47(13)
Ni1...Ni1 <sup>i</sup>	3.533(1)	Cl1-Ni1-Cl2 <sup>i</sup>	152.29(7)
N2-Ni1-N1	81.6(2)	Cl2-Ni1-Cl2 <sup>i</sup>	84.23(5)
N2-Ni1-Cl1	107.32(13)	Ni1-Cl2-Ni1 <sup>i</sup>	95.77(5)
N1-Ni1-Cl1	93.35(13)		
(i) -x+1,-y+2,-z+2			

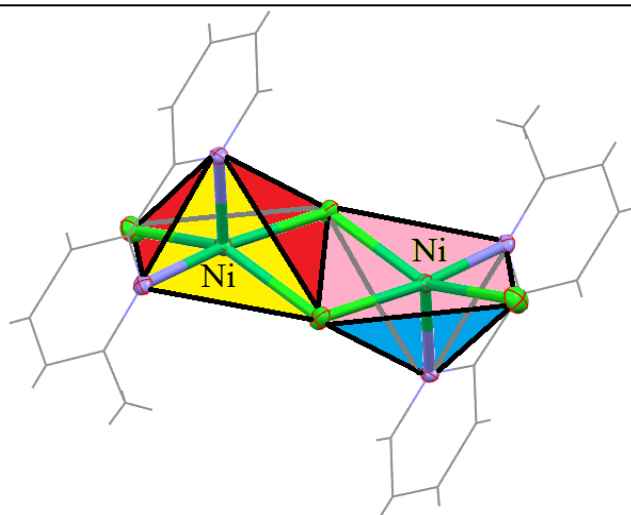


Fig. 4: The coordination polyhedral of  $[\text{NiCl}(6\text{-mbipy})]_2(\mu\text{-Cl})_2$  (**1**).

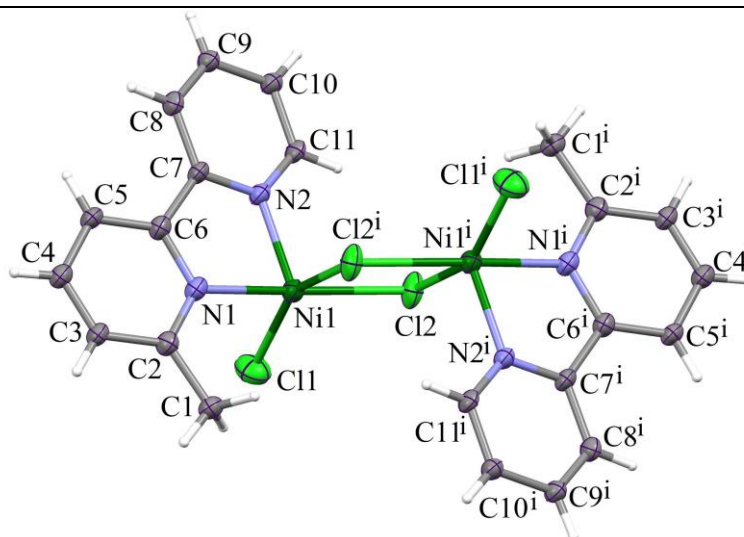


Fig. 5: The labeled diagram of  $[\text{NiCl}(6\text{-mbipy})]_2(\mu\text{-Cl})_2$  (**1**). Thermal ellipsoids are at the 30% probability level. Symmetry code: (i)  $-x+1, -y+2, -z+2$ .

## CONCLUSIONS

In this paper, a new binuclear complex of  $[\text{NiCl}(6\text{-mbipy})]_2(\mu\text{-Cl})_2$  (**1**) has been synthesized. This complex was characterized by spectroscopic methods and its structure was determined by the single crystal diffraction analysis. This compound is centrosymmetric binuclear complex and the coordination geometry around each central metal is five-coordinated in a distorted square-pyramidal configuration. Furthermore, the luminescence emission of **1** was blue shifted and is stronger than that of free 6-methyl-2,2'-bipyridine ligand.

Thermal stabilities of **1** was also studied by thermogravimetric analysis.

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## Supplementary Material

Crystal chemical information has been deposited with the Cambridge Structural Database under number CCDC

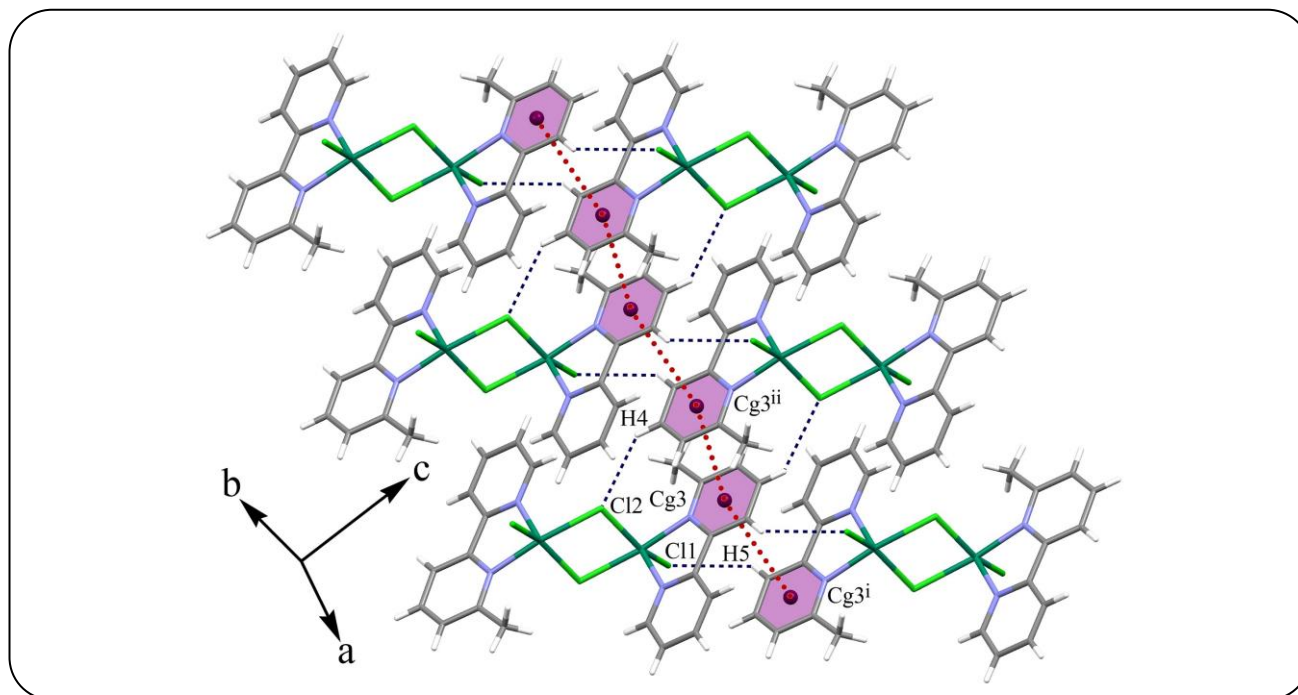


Fig. 6: Crystal packing diagram for  $[\text{NiCl}(6\text{-mbipy})]_2(\mu\text{-Cl})_2$  (1). Intermolecular C-H...Cl hydrogen bonds and  $\pi\cdots\pi$  contacts are shown as dashed lines. Symmetry codes: (i)  $-x, 2-y, 1-z$ ; (ii)  $1-x, 2-y, 1-z$ .

1587366, from where it can be obtained free of charge on request at the following website:  
[www.ccdc.cam.ac.uk/products/csd/faqs](http://www.ccdc.cam.ac.uk/products/csd/faqs).

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