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**NICKEL(II) COMPLEX CONTAINING 5,5'-DIMETHYL-2,2'-BIPYRIDINE:
CRYSTAL STRUCTURE AND LUMINESCENT PROPERTIES****A. Abedi¹, E. Saemian¹, V. Amani²**¹*Department of Chemistry, North Tehran Branch, Islamic Azad University, P.O. Box: 19585-936, Tehran, Iran
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[Ni(5,5'-dmbipy)₂Cl₂]·3H₂O (**1**) complex was obtained from the reaction of NiCl₂·6H₂O with 5,5'-dimethyl-2,2'-bipyridine (5,5'-dmbipy) in a mixture of CH₃OH/CH₃CN. This complex was characterized by elemental analysis, IR, UV-Vis and luminescence spectroscopy, and its structure was determined by the single-crystal diffraction method. The Ni atom has a distorted octahedral coordination by four N atoms from two 5,5'-dmbipy ligands and two Cl⁻ anions.

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Keywords: nickel(II), 5,5'-dimethyl-2,2'-bipyridine, crystal structure, luminescent properties.**INTRODUCTION**

Nickel, a group 10 element, has the electronic configuration 3d⁸ and exists chiefly in the +2 oxidation state. However, nickel compounds in the other oxidation states -1, 0, +1, +3, +4 are also known. Ni²⁺ generally forms octahedral and square planar complexes [1]. During last decade several nickel(II) complexes with N donor ligands were reported and were characterized by spectroscopy and X-ray diffraction method [2—8]. The nickel(II) complexes with N donor ligands are interest owing to their importance for catalysts [9, 10]. 5,5'-Dimethyl-2,2'-bipyridine (5,5'-dmbipy) is a good bidentate ligand, and numerous complexes have been prepared with it, such as those of iron [11], platinum [12], vanadium [13], lead [14], mercury [15], gold [16], cadmium [17], zinc [18], indium [19], thallium [20] and rhenium [21]. We report herein the synthesis, characterization and crystal structure of a new nickel (II) complex with chloride and 5,5'-dimethyl-2,2'-bipyridine. It is notable that complex **1** is the first complex containing chloride and 5,5'-dimethyl-2,2'-bipyridine ligand, and the crystal structure of [Ni(5,5'-dmbipy)₂(N₃)₂]·H₂O has been reported previously [22].

EXPERIMENTAL

Materials and physical methods. All chemicals were purchased from Merck and Aldrich. Infrared spectra (4000—250 cm⁻¹) of solid samples were taken as 1 % dispersion in CsI pellets using a Shimadzu-470 spectrometer. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer. Melting point was obtained with a Kofler Heizbank Rechart type 7841 melting point apparatus, UV-Vis spectra were recorded on a Specord S600 spectrometer using a 1 cm path length cell in methanol at room temperature, luminescence spectra were recorded on a Perkin Elmer LS45 using a 1 cm path length.

Synthesis of $[\text{Ni}(\text{5,5'-dmbipy})_2\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ (1**).** A solution of 5,5'-dimethyl-2,2'-bipyridine (0.56 g, 3.00 mmol) in acetonitrile (10 ml) was added to a solution of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (0.36 g, 1.50 mmol) in methanol (15 ml) and the resulting green solution was stirred for 30 min at 45 °C. After one week, green prismatic crystals of **1** were isolated (yield 0.63 g, 76 %, m. p. > 300 °C). IR (CsI, cm^{-1}): 3378br, 3045w, 2940w, 1627s, 1479s, 1392m, 1315w, 1244s, 1159m, 1051s, 996w, 839s, 732m, 643m, 581w, 512w, 427m, 319m, 264m. UV-Vis: λ_{max} (CH_3OH , nm), 253, 305, 317, 550, 960. Anal. Calcd. (%) for $\text{C}_{24}\text{H}_{30}\text{Cl}_2\text{N}_4\text{NiO}_3$: C 52.21, H 5.43, N 10.14. Found (%): C 51.81, H 5.39, N 10.06.

Crystallographic data collection and structure determination. The X-ray diffraction measurements were made on a Bruker APEX II CCD area detector diffractometer at 298 K (MoK_α radiation, graphite monochromator, $\lambda = 0.71073 \text{ \AA}$). The structure of **1** was solved by SHELX-97 and an absorption correction was done using the SADABS programs [23]. Data collection, cell refinement, and data reduction were done by APEX II, SAINT, SHELXTL, PLATON, and MERCURY [23–26].

RESULT AND DISCUSSION

Synthesis and characterization. Complex **1** was obtained by the reaction of one equivalent of $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ with two equivalent of 5,5'-dimethyl-2,2'-bipyridine in a mixture of $\text{CH}_3\text{OH}/\text{CH}_3\text{CN}$ at 45°.

Spectroscopic characterization of $[\text{Ni}(\text{5,5'-dmbipy})_2\text{Cl}_2]\cdot 3\text{H}_2\text{O}$ (1**).** IR absorptions of **1** are listed in the experimental section and contain several bands between 500 cm^{-1} and 3100 cm^{-1} , which are related to the hetero aromatic ring modes C—H, C=C, C=N, C—C, and C—N [12, 27–30]. These bands are shifted to higher frequencies upon coordination in complex of **1** [12, 27–30]. This shift to higher frequencies upon coordination has been observed for bipyridine and its derivatives [12, 27–30], and can be explained by changing the conformation of the free ligand from *anti* in a free ligand to *syn* orientation in the complexed state. The vibration bands around 3045 cm^{-1} and 2940 cm^{-1} are assigned to $\nu(\text{C—H}_{\text{cycle}})$ and $\nu(\text{C—H}_{\text{Me}})$, respectively. The broad band near 3378 cm^{-1} can be assigned to $\nu(\text{O—H})$ vibrations [28]. Far infrared spectrum of complex **1** was recorded between 400 cm^{-1} and 260 cm^{-1} . The Ni—N and Ni—Cl stretching vibrations appear at 264 cm^{-1} and 319 cm^{-1} , respectively [28].

UV-Vis spectrum was recorded in the 200–1100 nm range in methanol. The intense bands at higher energy near-UV region, 253 nm, 305 nm, and 317 nm, are assigned to intra-ligand $\pi^*\rightarrow\pi$ transitions of 5,5'-dmbipy. The visible and near IR regions also contain two broad bands with low intensity absorbance at 550 nm and 960 nm, which are assigned to *d—d* transition [3, 31] (Fig. 1).

The luminescence emission spectra ($\lambda_{\text{ex}} = 315 \text{ nm}$) of 5,5'-dmbipy and **1** were obtained in DMSO at room temperature and the results are displayed in Fig. 2. The maximum emission of 5,5'-dmbipy at

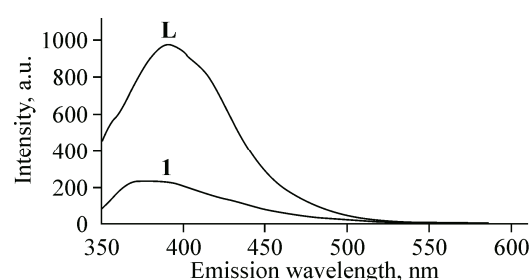
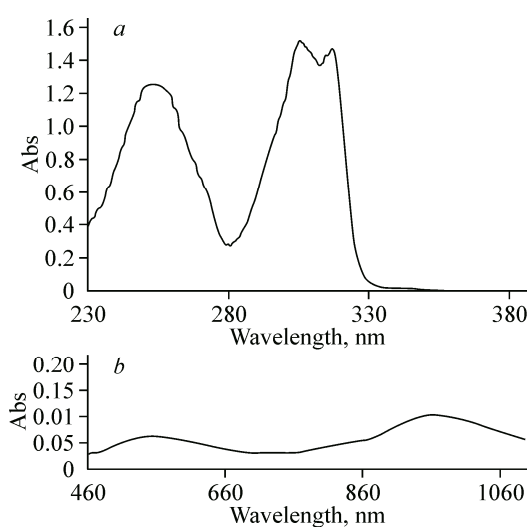


Fig. 1 (left). UV-Vis absorption spectrum of **1** (a, c = $1.15 \times 10^{-5} \text{ M}$, b, c = $4.65 \times 10^{-4} \text{ M}$) in CH_3OH

Fig. 2 (right). The luminescence spectra of **L** ($4.52 \times 10^{-3} \text{ M}$) and **1** ($4.60 \times 10^{-3} \text{ M}$) in CH_3OH at room temperature; excitation wavelength = 315 nm

Table 1

Crystallographic and structure refinement data for 1

Formula	$C_{24}H_{30}Cl_2N_4NiO_3$
Formula weight	552.11
Temperature, K	298(2)
Wavelength λ , Å	0.71073
Crystal system	Monoclinic
Space group	$C2/c$
Crystal size, mm	0.10×0.12×0.22
a, b, c , Å; β , deg.	18.1953(17), 14.0261(12), 11.9338(12); 121.689(6)
Volume, Å ³	2591.6(5)
Z	4
Density (calc.), g/cm ³	1.415
θ ranges for data collection	1.96—26.00
$F(000)$	1152
Absorption coefficient, mm ⁻¹	0.987
Index ranges	$-22 \leq h \leq 19$, $-15 \leq k \leq 17$, $-14 \leq l \leq 14$
Data collected	6752
Unique data (R_{int})	2550, (0.064)
Completeness to θ , %	99.8
Parameters, restraints	184, 0
Final R_1 , wR_2 (obs. data)	0.0497, 0.0834
Final R_1 , wR_2 (all data)	0.0950, 0.1027
Goodness of fit on F^2 (S)	1.012
Largest diff peak and hole, e/Å ³	0.332, -0.268

400 nm is shifted to 376 nm in complex **1**, with blue-shift after coordination to Ni(II) (24 nm blue-shifted compared to the related emission band). The similarity of the shapes of the emission spectra of 5,5'-dmbipy and **1** suggests their equal origins, which can be from ligand centered transitions (LC), such as $\pi^* \rightarrow \pi$ emission. The observed blue-shift for **1** can be explained by a decrease of the energy gap between the ground and excited states in the 5,5'-dmbipy ligand upon complexation with Ni(II) [32—35].

Description of the molecular structure of [Ni(5,5'-dmbipy)₂Cl₂]·3H₂O (1). Crystallographic data for **1** are given in Table 1 and the selected bond lengths and angles are presented in Table 2. The ORTEP view with the numbering schemes for compound **1** is shown in Fig. 3. The asymmetric unit of the title compound contains one half of the crystallographically independent [Ni(5,5'-dmbipy)₂Cl₂] molecule and one and half water solvent molecules. In the title complex, the Ni atom has a distorted octahedral coordination by four N atoms from two 5,5'-dimethyl-2,2'-bipyridine ligands and two Cl⁻ anions.

Table 2

Bond distances (Å) and bond angles (deg.) for 1

Ni1—Cl1	2.4266(10)	Cl1—Ni1—N1	96.67(7)	Cl1—Ni1—N2a	88.80(7)	N1—Ni1—N2a	92.37(11)
Ni1—N1	2.074(3)	Cl1—Ni1—N2	174.63(9)	N1—Ni1—N2	78.36(11)	N2—Ni1—N2a	93.42(10)
Ni1—N2	2.109(3)	Cl1—Ni1—Cl1a	89.43(4)	N1—Ni1—N1a	166.57(12)	Cl1a—Ni1—N1a	96.67(7)
		Cl1—Ni1—N1a	92.87(7)				

Symmetry code: (a) $1-x, y, 1/2-z$.

Fig. 3. The labeled diagram of **1**. Thermal ellipsoids are at 30 % probability level

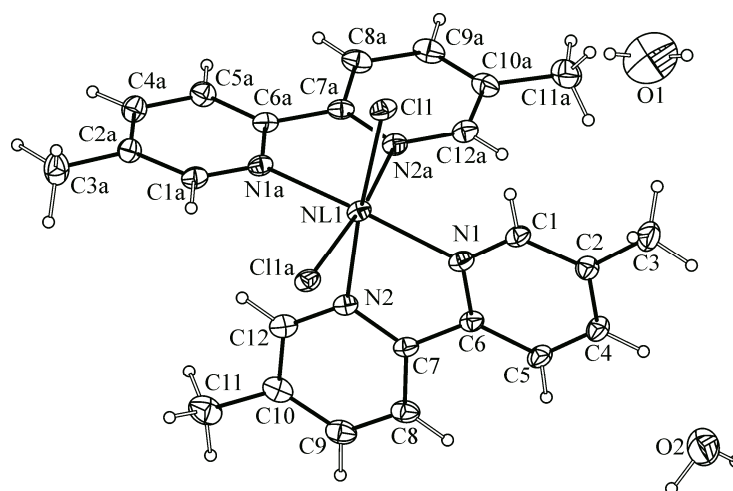
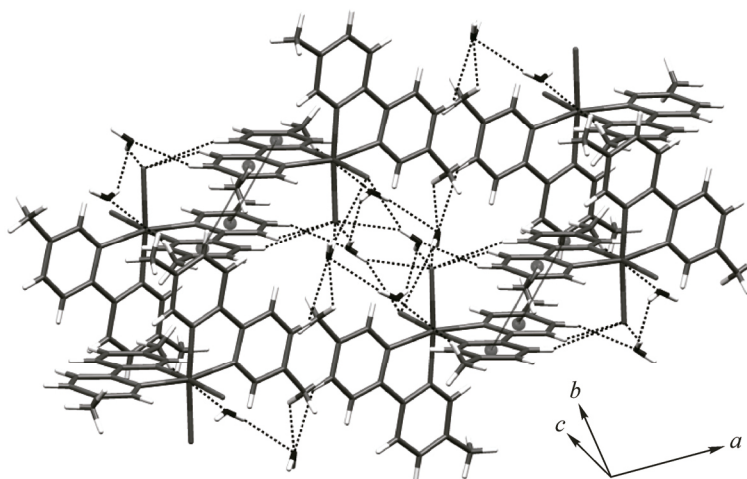


Fig. 4. Crystal packing diagram for **1**. Intermolecular O—H···O, O—H···Cl, C—H···Cl and C—H···O hydrogen bonds are shown as dashed lines



The Ni—N bond lengths are 2.074(3) Å and 2.109(3) Å, and Ni—Cl bond length is 2.4266(10) Å (Table 2). The Ni—N and Ni—Cl bond lengths and angles are in good agreement with the corresponding values in $[\text{Ni}(\text{bipy})_2\text{Cl}_2]\cdot\text{CH}_3\text{OH}$ [36]. The pyridine rings in the title complex are slightly distorted from planarity. The mean planes of rings $A(\text{N}1/\text{C}1\text{—}\text{C}2/\text{C}4\text{—}\text{C}6)$, $B(\text{N}2/\text{C}7\text{—}\text{C}10/\text{C}12)$ and $C(\text{N}1/\text{N}1/\text{C}6\text{—}\text{C}7/\text{N}2)$ make the following dihedral angles with each other: $A/B = 5.11^\circ$, $A/C = 3.93^\circ$ and $B/C = 3.18^\circ$. This distortion from planarity is due to the steric hindrance caused by the methyl group.

In the crystal structure of complex **1**, Fig. 4, it seems that the main factors controlling the packing of the structure are intermolecular C—H···Cl and C—H···O hydrogen bonds (Table 3) and $\pi\text{—}\pi$ interactions between the pyridine rings, $\text{C}g^3\cdots\text{C}g^{4^i}$ ($i = 1/2-x, 1/2-y, -z$; centroid-centroid distance is

Table 3

Hydrogen bond geometry for **1** in crystal packing (Å, deg.)

D—H···A	D—H	H···A	D···A	D—H···A	Symmetry code
O1—H1B···O2	0.78(8)	2.30(8)	2.977(12)	146(6)	$1/2-x, 1/2-y, 1-z$
O2—H2A···Cl1	0.95(10)	2.35(10)	3.243(7)	156(10)	$-1/2+x, 1/2-y, -1/2+z$
O2—H2B···Cl1	0.80(11)	2.73(12)	3.388(8)	142(10)	$1/2-x, -1/2+y, 1/2-z$
C1—H1···Cl1	0.9300	2.7800	3.410(4)	126.00	—
C4—H4···O2	0.9300	2.5500	3.285(9)	136.00	—

3.740(2) Å) [Cg3 and Cg4 are centroids of the rings (N1/C1—C2/C4—C6) and (N2/C7—C10/C12), respectively].

CCDC 995694 contains the supplementary crystallographic data for **1**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk.

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REFERENCES

1. Riedel E. *Anorganische Chemie*, 6th ed., De Gruyter, 2004.
2. Hipler B., Döring M., Dubs C., Görts H., Hübler T., Uhlig E. // *Z. Anorg. Allg. Chem.* – 1998. – **624**. – P. 1329 – 1335.
3. Ferbinteanu M., Cimpoesu F., Andruh M., Rochon F.D. // *Polyhedron*. – 1998. – **17**. – P. 3671 – 3679.
4. Malecki J.G., Machura B., Świtlicka A. // *Struct. Chem.* – 2011. – **22**. – P. 77 – 87.
5. Ye B.H., Chen X.M., Xue G.Q., Ji L.N. // *J. Chem. Soc., Dalton Trans.* – 1998. – P. 2827 – 2831.
6. Rujiwatra A., Yimklan S., Prior T.J. // *Polyhedron*. – 2012. – **31**. – P. 345 – 351.
7. Pérez C.R., Lorenzo L.P.A., Lloret F., Julve M. // *Inorg. Chim. Acta*. – 2002. – **336**. – P. 131 – 136.
8. Janiak C., Deblon S., Wu H.P., Kolm M.J., Klüfers P., Piotrowski H., Mayer P. // *Eur. J. Inorg. Chem.* – 1999. – P. 1507 – 1521.
9. Massicot F., Schneider R., Fort Y., Illy-Cherrey S., Tillement O. // *Tetrahedron*. – 2001. – **57**. – P. 531 – 536.
10. Kinnunen T.J.J., Haukka M., Pakkanen T.T., Pakkanen T.A. // *J. Organomet. Chem.* – 2000. – **613**. – P. 257 – 262.
11. Amani V., Safari N., Khavasi H.R. // *Polyhedron*. – 2007. – **26**. – P. 4257 – 4262.
12. Amani V., Safari N., Khavasi H.R., Akkurt M. // *Polyhedron*. – **28**. – P. 3026 – 3030.
13. Ostad S.N., Emadi S.M., Tavajohi S., Amani V., Abedi A. // *Bull. Korean Chem. Soc.* – 2012. – **33**, N 11. – P. 3891 – 3894.
14. Alizadeh R., Amani V. // *Struct. Chem.* – 2011. – **22**. – P. 1153 – 1163.
15. Alizadeh R., Amani V., Farshady A.A., Khavasi H.R. // *J. Coord. Chem.* – 2010. – **63**. – P. 2122 – 2131.
16. Karaca S., Akkurt M., Safari N., Amani V., Büyükgüngör O., Abedi A. // *Acta Crystallogr.* – 2009. – **E65**. – P. m335 – m336.
17. Ahmadi R., Kalateh K., Amani V. // *Acta Crystallogr.* – 2010. – **E66**. – P. m562.
18. Khalighi A., Ahmadi R., Amani V., Khavasi H.R. // *Acta Crystallogr.* – 2008. – **E64**. – P. m1211 – m1212.
19. Kalateh K., Ahmadi R., Ebadi A., Amani V., Khavasi H.R. // *Acta Crystallogr.* – 2008. – **E64**. – P. m1353 – m1354.
20. Ghiasi Z., Amani V., Mirzaei P., Safari N., Abedi A. // *Aust. J. Chem.* – 2013. – **66**. – P. 676 – 684.
21. Perera T., Abhayawardhana P., Fronczek F.R., Marzilli P.A., Marzilli L.G. // *Eur. J. Inorg. Chem.* – 2012. – P. 618 – 627.
22. Phatchimkun J., Kongsaree P., Suchaichit N., Chaichit N. // *Acta Crystallogr.* – 2009. – **E65**. – P. m1020 – m1021.
23. Sheldrick G.M. SADABS, Bruker AXS. – Madison, WI, USA, 1998.
24. Bruker SMART and SAINT. Bruker AXS Inc. – Madison, WI, USA, 1998.
25. Sheldrick G.M. // *Acta Crystallogr.* – 2008. – **A64**. – P. 112 – 122.
26. Mercury 1.4.1. Copyright Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK, 2001–2005.
27. Amani V., Safari N., Khavasi H.R. // *Polyhedron*. – 2007. – **26**. – P. 4257 – 4262.
28. Nakamoto K. *Infrared and Raman spectra of inorganic and coordination compound, Part B: Application in coordination, organometallic and bioinorganic chemistry.* – New York: John Wiley and Sons Inc., 2009.
29. Amani V., Safari N., Khavasi H.R., Mirzaei P. // *Polyhedron*. – 2007. – **26**. – P. 4908 – 4914.
30. Amani V., Safari N., Notash B., Khavasi H.R. // *J. Coord. Chem.* – 2009. – **62**. – P. 1939 – 1950.
31. Harris C.M., McKenzie E.D. // *J. Inorg. Nucl. Chem.* – 1967. – **29**. – P. 1047 – 1068.
32. Abedi A., Safari N., Amani V., Khavasi H.R. // *J. Coord. Chem.* – 2012. – **65**. – P. 325 – 338.
33. Abedi A., Amani V., Safari N. // *Main Group Chem.* – 2012. – **11**. – P. 223 – 233.
34. Liu S.G., Zuo J.L., Li Y.Z., You X.Z. // *J. Mol. Struct.* – 2004. – **705**. – P. 153 – 157.
35. Modi C.K., Jani D.H., Patel H.S., Pandya H.M. // *Spectrochim. Acta, Part A*. – 2010. – **75**. – P. 1321 – 1328.
36. Fontaine F.G. // *Acta Crystallogr.* – 2001. – **E57**. – P. m270 – m271.