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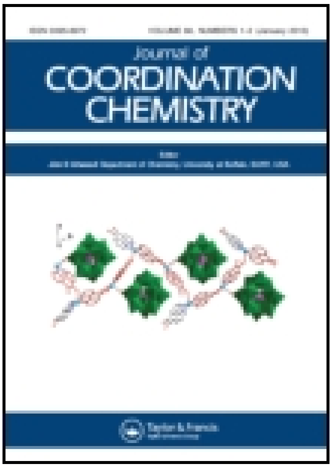

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Preparation, structures, and properties of nickel complexes containing 2,6-bis[4′,4′-dimethyloxazolin-2′-yl]pyridine, a pincer ligand

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Preparation, structures, and properties of nickel complexes containing 2,6-bis[4′,4′-dimethyloxazolin-2′-yl]pyridine, a pincer ligand

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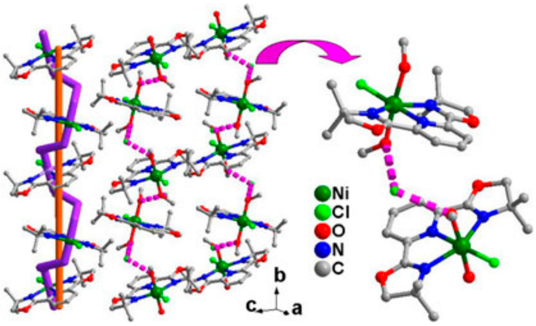

Five- and six-coordinate nickel complexes [(Dm-Pybox)NiCl$_2$], [(Dm-Pybox)Ni(H$_2$O)Cl$_2$], [(Dm-Pybox)Ni(H$_2$O)$_2$Cl]Cl (**2a**), and [(Dm-Pybox)Ni(MeOH)$_2$Cl]Cl (**2b**), where Dm-Pybox is 2,6-bis[4′,4′-dimethyloxazolin-2′-yl]pyridine, have been isolated and structurally characterized by single crystal X-ray diffraction. The solid state structures of **2a** and **2b** feature different modes of non-covalent interactions, C–H···Cl, C–H···O and O–H···Cl interactions. Spectroscopic and analytical methods, UV–vis and thermogravimetric analyses were done to further investigate chemical properties of the complexes.

Keywords: Pincer; Nickel; Synthesis; Structure; Non-covalent interactions

1. Introduction

Tridentate oxazoline-based pincer ligands in which the central pyridine- or benzene-based ring containing oxazoline substituent in the two ‘flanking’ ortho positions have been used in transition metal chemistry [1–4]. Oxazoline-based pincer ligands and their congeners

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*Corresponding author. Email: wgjiasy@mail.ahnu.edu.cn have been employed in homogeneous and asymmetric catalysis [5]. Although pincer Ni complexes of the form PNP and NNN have been widely used in C–C, C–S bond formation and carbon dioxide reduction [6–9], catalytic applications of oxazoline-based pincer nickel complexes are still relatively unexplored.

Hydrogen bond interactions play a dominant role in supramolecular architectures due to their selectivity and directionality [10]. Non-classical H-bonding between a non-polar C–H unit with suitable H-bond acceptors, for instance C–H···X (X=O, N, S, F, Cl, Br or I), is observed in organic and organometallic compounds [11]. Such non-classical C–H···X interactions are weaker than O–H···Cl and N–H···Cl interactions as the H-donor is much more electronegative [12]. Recent computational studies by Huang's group have found that weak but important C–H···X interactions enable organocatalysts to install high enantioselectivity for organic reactions [13]. X-ray studies on the complexes offer similar insights and significance to C–H···Cl interaction playing a fundamental role in supramolecular assembly [14]. The para C–H pyridyl position of pincer ligands behaving as H-donors in self-assembly of supramolecular structures is unreported. In this work, we report the synthesis and characterization of a series of five- and six-coordinate Ni(II) complexes containing Dm-Pybox pincer ligand ($[(\text{Dm-Pybox})\text{Ni}]^{2+}$). Solid state structures of the complexes were obtained with single crystal X-ray diffraction. A number of factors appear to influence the preference for particular systems to form either five- or six-coordinate complexes, and discussion is provided herein.

2. Experimental

2.1. *Materials and measurements*

All manipulations were carried out under nitrogen using standard Schlenk and vacuum-line techniques. All solvents were purified and degassed by standard procedures. The 2,6-bis[4′,4′-dimethyloxazolin-2′-yl]pyridine (**Dm-pybox**) was synthesized according to procedures described [15]. Other chemicals were analytical grade and used as received. IR spectra were recorded on a Niclolet AVATAR-360IR spectrometer. Elemental analyses were performed on an Elementar III vario EI Analyzer. Thermogravimetric analyses (TGA) were taken on a Shimadzu simultaneous TGA/DTA analyzer DTG-60A. The UV measurements were carried out on a Hitachi U-3010 UV–vis spectrophotometer.

2.2. *Preparation of the complex*

2.2.1. Synthesis of (Dm-Pybox)NiCl$_2$ (1). In a 100 mL-round-bottomed flask was placed Dm-pybox (**1a**) (273 mg, 1 mM), $(\text{PPh}_3)_2\text{NiCl}_2$ (654 mg, 1 mM), and 40 mL CH_2Cl_2. The mixture was stirred at room temperature overnight and then the solvent was removed with a rotary evaporator; the resulting solid was washed with Et_2O and then dried *in vacuo*. The product was recrystallized from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ to give orange crystals. Yield: (302 mg, 74%). Anal. Calcd for $\text{C}_{15}\text{H}_{19}\text{Cl}_2\text{N}_3\text{NiO}_2$ (%):C, 44.71; H, 4.75; N, 10.43. Found: C, 43.50; H, 4.66; N, 10.35. IR (KBr cm^{-1}):3392 (m), 3055 (m), 1739 (m), 1653 (s), 1635 (m), 1525 (m), 1508 (m), 1463 (m), 1404 (m), 1380 (w), 1205 (s), 945 (m), 673 (m).

2.3. *X-ray structure determination*

Diffraction data of **2a** and **2b** were collected on a Bruker AXS SMART APEX diffractometer, equipped with a CCD area detector using Mo Kα radiation ($\lambda = 0.71073$ Å). All the data were collected at 102 K, and the structures solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares (SHELXL) [16]; SADABS [17] absorption corrections were applied to the data, all non-hydrogen atoms were refined anisotropically, and hydrogens were located at calculated positions. All calculations were performed using the Bruker Smart program. A summary of crystallographic data and selected experimental information are given in table 1 and selected bond lengths and angles are shown in Supplementary material (see online supplemental material at http://dx.doi.org/10.1080/00958972.2014.886109). Hydrogen bond lengths and angles for **2a** and **2b** are shown in Supplementary material.

3. Results and discussion

3.1. *Structural description of 1*

When $(PPh_3)_2NiCl_2$ was treated with Dm-Pybox pincer ligand in CH_2Cl_2 at room temperature in air, orange crystals of (Dm-Pybox)$NiCl_2$ (**1**) were isolated in moderate yields (74%)

Table 1. Crystallographic data and structure refinement parameters for **2a** and **2b**.

	2a	**2b**
Empirical formula	$C_{15.50}H_{23}Cl_3N_3NiO_{3.50}$	$C_{17}H_{27}Cl_2N_3NiO_4$
Formula weight	472.43	467.03
Crystal system, Space group	Triclinic, *P*-1	Monoclinic, *P2₁/c*
a (Å)	10.9290(6)	10.2893(17)
b (Å)	11.5851(6)	11.6289(19)
c (Å)	18.1830(9)	18.005(3)
α (°)	94.1210(10)	90
β (°)	99.5400(10)	100.394(3)
γ (°)	112.4330(10)	90
Volume (Å^3), Z	2075.39(19), 4	2119.0(6), 4
D_{Calcd} (mg/m^3)	1.512	1.464
μ (Mo Kα) (mm^{-1})	1.343	1.194
F (0 0 0)	976	976
θ Range (°)	2.19–27.41	2.77–27.49
Limiting indices	−14, 15; −15, 14; −23, 23	−11, 13; −10, 15; −22, 23
Reflections/unique [R(int)]	9504/8530 [0.0290]	4850/4413 [0.0204]
Completeness to θ (°)	27.50 (99.9%)	27.50 (99.5%)
Data/restraints/ parameters	9504/49/548	4850/3/258
Goodness-of-fit on F^2	1.027	1.073
Final R indices [($I > 2\sigma(I)$)][a]	$R_1 = 0.0403$, $wR_2 = 0.0958$	$R_1 = 0.0296$, $wR_2 = 0.0824$
R indices (all data)	$R_1 = 0.0450$, $wR_2 = 0.0991$	$R_1 = 0.0332$, $wR_2 = 0.0847$
Largest. diff. peak/hole (e/Å^{-3})	0.868/−0.572	0.583/−0.335

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o^2| - |F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

after recrystallization. NMR spectra of the complexes are not informative due to paramagnetism. This is also observed in other nickel complexes [18]. Complex **1** was fully characterized by IR and elemental analysis and the infrared spectrum exhibits intense C=N stretching of oxazoline at 1650 cm^{-1}.

3.2. *Structural description of 2a*

Two coordinated chlorides in **1** could be replaced by different solvent molecules, such as H_2O and MeOH; the five-coordinate nickel(II) complex **1** forms six-coordinate pincer nickel(II) complexes upon ligation. When an orange solution of **1** in CH_2Cl_2 was heated, the color turned pale green and upon cooling to ambient temperature, the solution turned orange again. Subsequently, green crystals were isolated and identified as six-coordinate $[(Dm\text{-}Pybox)Ni(H_2O)_2Cl]Cl$ or $[(Dm\text{-}Pybox)Ni(H_2O)Cl_2]$ (**2a**) by single-crystal X-ray diffraction (figure 1).

Complex **2a** crystallized in the triclinic space group *P*-1 with four molecules in the unit cell. Two independent octahedral isostructures exist in **2a**, one being $[(Dm\text{-}Pybox)Ni(H_2O)Cl_2]$, and the other, $[(Dm\text{-}Pybox)Ni(H_2O)_2Cl]Cl$. The solid-state structure shows that chlorides are hydrogen bonded to water in the crystal lattice. The behavior described is consistent with the equilibrium shown in scheme 1, where the equilibrium position depends on the solvation of water in solution or the solid state. In aqueous environment, chloride is readily displaced by water, favoring the formation of $[(Dm\text{-}Pybox)Ni(H_2O)Cl_2]$, and then $[(Dm\text{-}Pybox)Ni(H_2O)_2Cl]Cl$ when water excess. Removal of water favors the formation of the five-coordinate complex $[(Dm\text{-}Pybox)NiCl_2]$ (**1**).

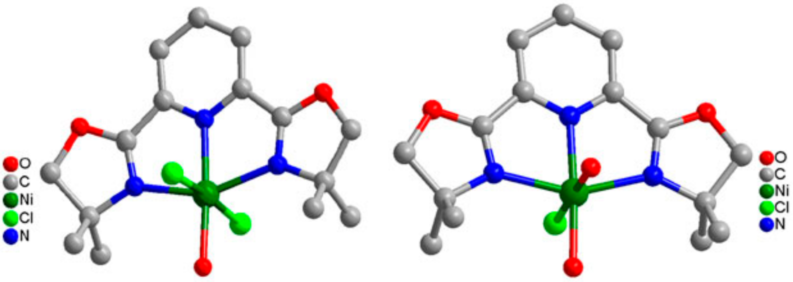
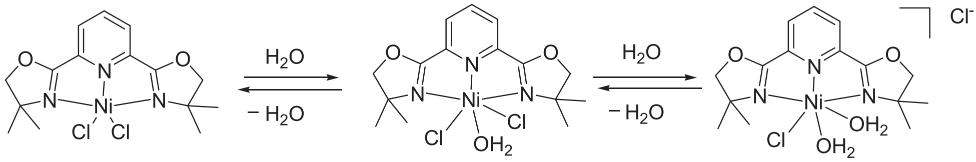


Figure 1. Molecular structure of **2a**; all hydrogens are omitted for clarity.

As seen in figure 2(a), intermolecular hydrogen bond between water on Ni and chloride [O(3w)···Cl(1) = 3.109(2) Å; O(1w)···O(3) = 3.089(3) Å] give a 2-D supramolecular grid structure in **2a**. Intermolecular O–H···Cl hydrogen bonds between water



Scheme 1. The ligand exchange in pincer nickel(II) complexes.

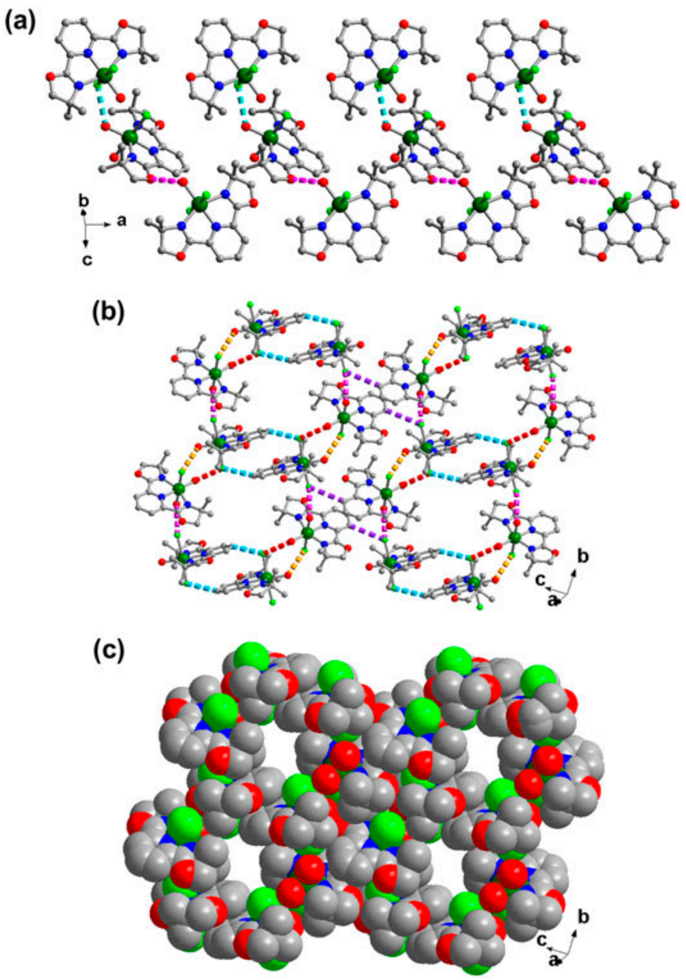


Figure 2. (a) 2-D structure of **2a**; (b) 3-D structure of **2a** mediated by intermolecular hydrogen bonding; (c) packing diagram for **2a**.

and chloride in **2a** [O···Cl = 3.064(2)–3.172(2) Å; O–H···Cl = 168(4)–175(2)°] and non-classical C–H···Cl intermolecular hydrogen bonds [C···Cl = 3.431(3)–3.724(3) Å; C–H···Cl = 126–174°] play crucial roles in the 3-D structure in the solid states. As shown in figure 2(c), the molecules stack to form channels due to intermolecular hydrogen bonds. A solvent CH_2Cl_2 is located in the channel hole with approximate dimensions of 6 Å × 3 Å.

3.3. *Structural description of 2b*

The dissolution of the orange (Dm-Pybox)$NiCl_2$ **1** in MeOH affords a pale-green solution which suggests possible chemical changes to the nickel center. Crystals of **2b** suitable for X-ray crystallographic diffraction were obtained by slow diffusion of diethyl ether into a concentrated solution of the complexes in CH_2Cl_2/MeOH. Complex **2b** crystallized in the

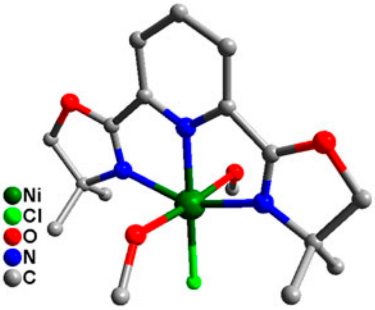


Figure 3. Molecular structure of **2b**; all hydrogens are omitted for clarity.

monoclinic space group $P2_1/c$, with four molecules in the unit cell. As shown in figure 3, **2b** possesses distorted octahedral coordination geometry around Ni, formed by three nitrogens of Dm-Pybox, two coordinated methanols and one Cl. The Ni deviates by 0.0131 Å out of the N(1)–N(2)–N(3) plane, while the chloride Cl(1) is almost coplanar with a deviation of 0.0376 Å. Two oxygens of coordinated methanol [O(3) and O(4)] occupy axial positions and form an angle of 174.97(49)° with the nickel core. Oxygens are nearly perpendicular to the equatorial plane with a dihedral angle of 88.13°. Its coordination geometry is similar to that observed in pincer nickel dichloride complexes [19].

As shown in figure 4, there are two forms of chlorides in the **2b** unit cell. One is coordinating to Ni and the other is non-coordinating Cl^-; both chlorides form O–H···Cl hydrogen bonds with adjacent molecules [O(3)···Cl(2) = 2.9906 Å; O(3)-H(3O)···Cl(2) = 172° and O(4)···Cl(2) = 2.9685 Å; O(4)–H(4O)···Cl(2) = 170°]. The molecular pincer Ni(II) units are linked into a helical chain along the *b*-axis via strong intermolecular hydrogen bonds. Two intertwined helical chains are generated around the crystallographic 2(1) axis with a pitch of 11.6289(19) Å, which is equal to the *b*-axis length. Each helix is linked by C–H···Cl intermolecular hydrogen bonds [C(17)···Cl(1) = 3.3558 Å; C(17)–H(17A)···Cl(1) = 124°] along the *a*-axis to form a 2-D architecture (figure 5).

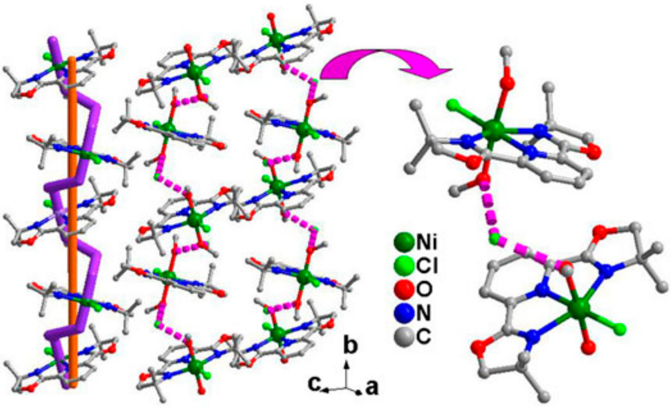


Figure 4. View of 1-D supramolecular helical polymeric chains in **2b** along the *b*-axis.

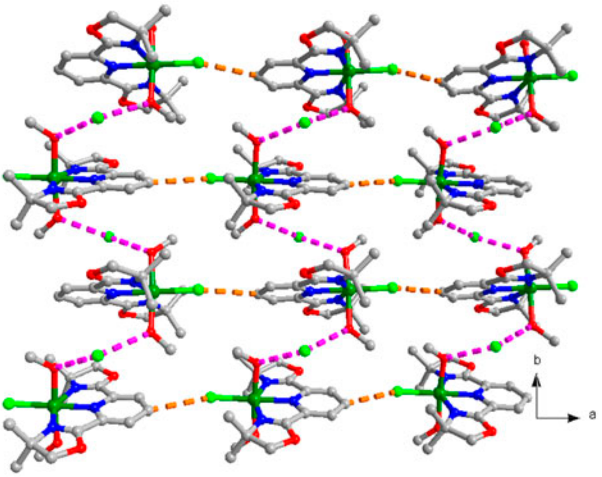


Figure 5. 2-D supramolecular structure of **2b** mediated by weak C–H···Cl hydrogen bonding along the *a*-axis.

3.4. *Coordination studies in solution*

In order to further investigate the binding of pincer Dm-Pybox to Ni(II), a Ni(II)$Cl_2(PPh_3)_2$ solution was added to a solution containing Dm-Pybox and this process was monitored by UV–vis spectra. The absorptions of Dm-Pybox in MeOH change rapidly upon addition of Ni(II). As depicted in figure 6, the peak at 280 nm attenuated and disappeared, while the peak at 218 nm increases with higher concentrations of Ni(II). A new band at 262 nm attributable to charge transfer between Dm-Pybox and Ni(II) appears. No differences were

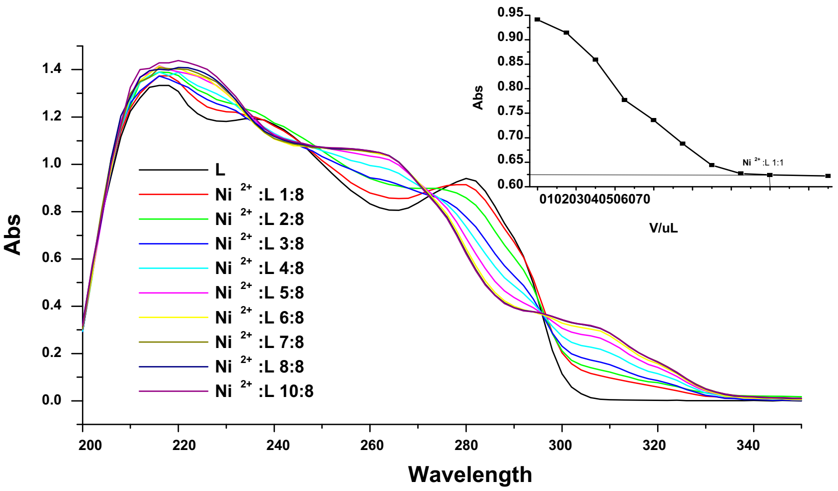


Figure 6. UV–vis titrations of Dm-Pybox (10^{-4} M/L in methanol) and Ni^{2+} (in methanol). Each spectrum was acquired after 15 min; the UV–vis titration of Dm-Pybox (10^{-4} M/L in methanol) and Ni^{2+} (in methanol); the Ni^{2+} (0.005 M/L) was added increasingly.

observed in the absorption spectra after the 1 : 1 ratio of Ni(II)/Dm-Pybox, so this experiment clearly indicates the formation of **2b**.

3.5. *Thermogravimetric analysis*

The thermal stability of **2a** and **2b** were also investigated through TGA (Supplementary material) from 30 to 800 °C under air with heating rate of 5 °C min^{-1}. The TGA curve reveals three weight losses for **2a** and **2b**. The first occurred between 30 and 110 °C and was attributed to loss of water. In the second step, both coordinated water and chloride for **2a** and methanol and chloride for **2b** were lost sequentially. Dm-Pybox starts to decompose gradually after 500 °C. From the TGA results, the complexes formed stable five-membered chelate rings, which may be attributed to highly polarized Ni–N and Ni–O bonds.

4. Conclusion

We have reported nickel complexes with pyridine-based pincer-type ligands. The chloride in **1** is labile and could be replaced by H_2O and MeOH forming six-coordinate pincer nickel(II) complexes. A combination of spectroscopic studies and X-ray crystallographic confirmed the structures of pincer nickel(II) complexes **2a** and **2b**.

Supplementary material

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Center, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-931249 (**2a**) and CCDC-931248 (**2b**) (Fax:+44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk; http://www.ccdc.cam.ac.uk). Selected bond lengths and angles are listed in the supplementary content.

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