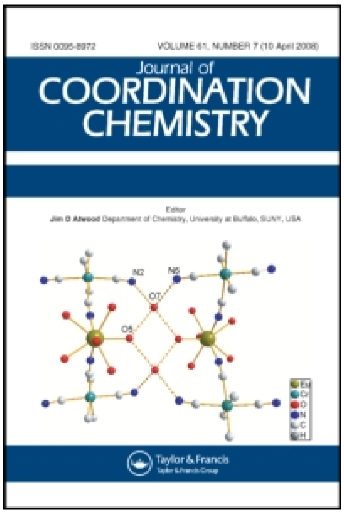

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, characterization, and crystal structure of a Ni(II) complex of an acyclic pentadentate Schiff base; an agreement between the experimental and theoretical results

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To cite this Article Salehzadeh, Sadegh , Golbedaghi, Reza and Khavasi, Hamid Reza(2009) 'Synthesis, characterization, and crystal structure of a Ni(II) complex of an acyclic pentadentate Schiff base; an agreement between the experimental and theoretical results', Journal of Coordination Chemistry, 62: 15, 2532 — 2539

To link to this Article: DOI: 10.1080/00958970902842489

URL: http://dx.doi.org/10.1080/00958970902842489

Journal of Coordination Chemistry
Vol. 62, No. 15, 10 August 2009, 2532–2539

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Synthesis, characterization, and crystal structure of a Ni(II) complex of an acyclic pentadentate Schiff base; an agreement between the experimental and theoretical results

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(*Received 6 November 2008; in final form 4 December 2008*)

A Ni(II) complex of an acyclic pentadentate Schiff base was prepared by template condensation of two equivalents of 2-acetylpyridine with one equivalent of *bis*(3-aminopropyl)amine in the presence of Ni(II) in methanol. The resulting complex, $[NiL_{33}(MeOH)](ClO_4)_2 \cdot CH_3OH$, was characterized by X-ray crystallography, elemental analysis, and IR spectrophotometry. The X-ray crystallographic structure revealed a six-coordinate, distorted octahedral geometry in which the sixth coordination being achieved by a methanol molecule. A theoretical study at DFT (B3LYP) level using standard 6-31G* basis set for ligand atoms and LanL2DZ for metal showed that the experimentally determined structure of the cation is about 8–20 kcal mol^{-1} more stable than its geometrical isomers.

Keywords: Schiff base; Pentadentate; Crystal structure; Theoretical studies

1. Introduction

Schiff-base complexes are an important area of research due to their simple synthesis, versatility, and diver applications [1, 2]. We have been interested in synthesis and characterization of macrocyclic and macroacyclic Schiff-base complexes and recently showed that in the presence of suitable metal ions, 2-acetylpyridine condenses with tripodal tetraamine ligands such as tris(3-aminopropyl)amine, tpt, and *bis*(3-aminopropyl)(2-aminoethyl)amine, ppe, in absolute MeOH to give a fully condensed Schiff-base complex [3]. However, in aqueous methanolic solution, the condensation is limited to a single step, and the metal complexes of the acyclic pentadentate mono-Schiff bases are produced [3–5]. The acyclic pentadentate Schiff-base ligands all belong to type (B) from the two known structural types (figure 1b). We previously reported the molecular structures of two Ni(II) complexes of type (B) acyclic pentadentate

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902842489

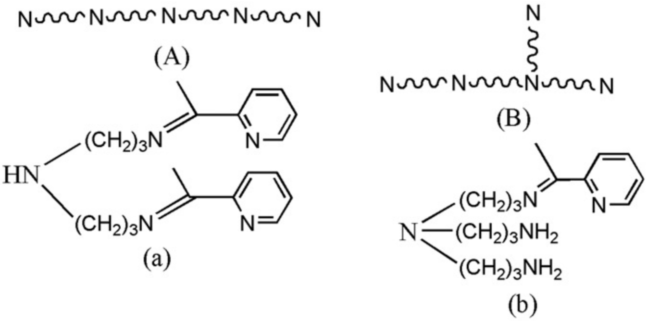


Figure 1. Two types of acyclic pentadentate (N5) Schiff-base ligands (upper); the structures of two examples for types (A) and (B), (a) and (b), respectively, of pentadentate Schiff-base ligands (lower).

Schiff-base ligands [3, 4]. In this work, we report condensation of *bis*(3-aminopropyl) amine with 2-acetylpyridine in the presence of Ni(II). In aqueous MeOH/EtOH the condensation is limited to a single step, while in the presence of a large excess of 2-acetylpyridine the expected fully condensed Schiff-base complex can be formed [6]. We now show that the latter, fully condensed Schiff-base complex can be easily formed through template condensation of *bis*(3-aminopropyl)amine with 2-acetylpyridine in the presence of Ni(II) in dry methanol. We also report the molecular structure of latter complex in which L (figure 1a) is an example of type (A) acyclic pentadentate Schiff-base ligands. Finally, a DFT study supports the observed molecular structure as the most stable one between the possible octahedral structures.

2. Experimental

2.1. *General information*

Bis(3-aminopropyl)amine, 2-acetylpyridine, and hydrated metal salt were obtained from Aldrich and used without purification. IR spectrum was measured on a Perkin Elmer FT-IRGX spectrophotometer.

2.2. *X-ray crystallography*

Suitable crystals of **1** were obtained by slow diffusion of diethyl ether vapor into a methanol solution. Crystal data and the major experimental parameters for the crystal structure of **1** are reported in table 1. A brown crystal of $0.50 \times 0.30 \times 0.25\,\text{mm}^3$ was mounted on a glass fiber and used for data collection. All measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 6,660 unique reflections. Data were collected at a temperature of 298(2) K to a maximum 2θ value of 54.2 in a series of ω-scans in 1° oscillations and integrated using the STOE X-AREA software package [7]. A numerical absorption correction was applied using X-RED [8] and X-SHAPE [9] software. The data were corrected for Lorentz and polarization effects. The structure

Table 1. Crystal data and refinement details of **1**.

Empirical formula	$C_{22}H_{35}Cl_2N_5NiO_{10}$
Formula weight	659.14
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P21/c$
Unit cell dimensions (Å, °)	
a	8.500(5)
b	16.719(7)
c	20.642(13)
α	90
β	97.21(5)
γ	90
V (Å^3)	2910(3)
Z	4
D_{Calcd} (mg m^{-3})	1.505
Absorption coefficient (mm^{-1})	0.910
$F(000)$	1376
Crystal size (mm^3)	0.50 × 0.30 × 0.25
θ range for data collection (°)	1.57 to 27.10
Index ranges	$-7 \leq h \leq 10$, $-21 \leq k \leq 19$ $-26 \leq l \leq 26$
R_{int}	0.1594
Completeness to $\theta = 27.10$	98.9%
Absorption correction	Numerical
Maximum and minium transmission	0.800 and 0.730
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6156/0/369
Goodness-of-fit on F^2	1.157
Final R indices	$R_1 = 0.0898$
$[I > 2\sigma(I)]$	$wR_2 = 0.1639$
R indices (all data)	$R_1 = 0.0926$, $wR_2 = 0.1821$
Largest difference peak and hole (e Å^{-3})	0.898 and −0.578

was solved by direct methods [10] and subsequent difference Fourier map and then refined on F^2 by full-matrix least-squares using anisotropic displacement parameters [9]. The N3 and O10 hydrogens were located in a difference map and their positions were freely refined. Other hydrogens were refined using a riding model (C–H = 0.93–0.97 Å) with their displacement parameters set at 1.2 times U_{eq} of the parent atom.

2.3. *Computational method*

The geometry of the cation in **1**, $[\text{NiL(MeOH)}]^{2+}$, as determined by X-ray crystal structure analysis (see figures 2 and 3 isomer **I**) was fully optimized in the gas phase at both the Hartree–Fock and DFT (B3LYP) [11] levels of theory using the Gaussian 98 program [12]. The geometries of other isomers [figure 3 (**II**), (**III**), and (**IV**)] were also fully optimized at the B3LYP level of theory. The atomic coordinates of **1** in its crystal structure were used for corresponding *ab initio* calculations on isomer **I** using the standard LanL2MB basis set on the whole complex, or standard 3-21G* or 6-31G* basis sets [13–15] for ligand atoms, and LanL2DZ for metal ion [16]. For isomers **II**–**IV**, a semiempirical structure was obtained by Hyperchem 5.02 [17] and was used for DFT calculations using all above basis sets, except 3-21G*. Calculations were performed on a Pentium-PC computer with a 4400 MHz processor.

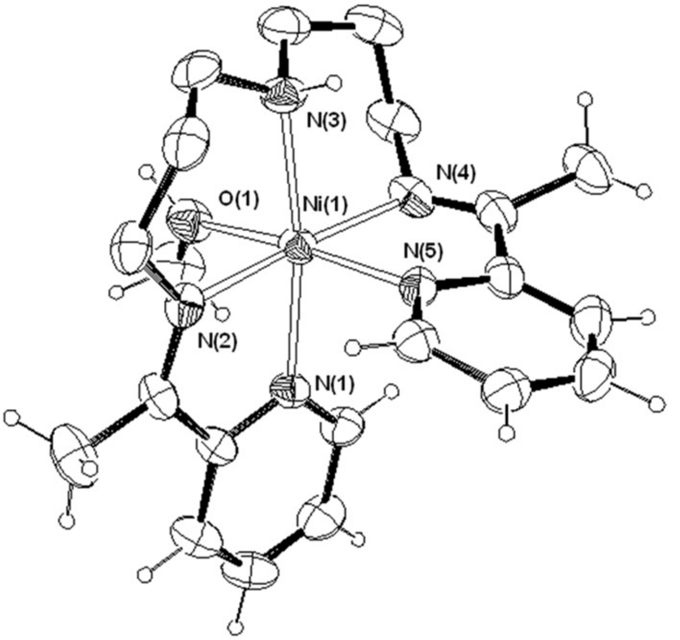
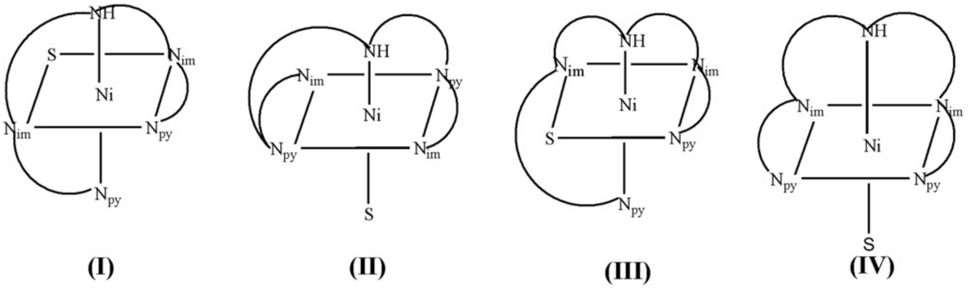


Figure 2. ORTEP view of X-ray crystal structure of **1**. Hydrogen atoms of methylene groups, as well as solvated MeOH molecule and perchlorate anions are omitted for clarity.



(I) (II) (III) (IV)

Figure 3. The schematic representation of isomers **I**–**IV** for $[NiL_{33}(MeOH)]^{2+}$. S represents the coordinated methanol molecule.

2.4. *Synthesis*

2.4.1. Synthesis of $[NiL_{33}(MeOH)](ClO_4)_2 \cdot MeOH$ (1). 2-Acetylpyridine (0.484 g, 4 mmol) and $Ni(ClO_4)_2$ (0.734 g, 2 mmol) dissolved in MeOH (5 mL) were added to a solution of *bis*(3-aminopropyl)amine (0.262 g, 2 mmol) in absolute MeOH (50 mL). The resulting solution was heated under reflux and stirred for 36 h; during this time it changes to brown. The solution was filtered and the filtrate was reduced to *ca* 10 cm^3. Crystalline compound was obtained by slow diffusion of Et_2O vapor into this solution. Yield: 0.4 g (31%) of **1**. Anal. Calcd for $C_{22}H_{35}Cl_2N_5NiO_{10}$ (%): C, 40.2; H, 5.37; N, 10.66. Found (%): 39.92; 5.32; 10.58. IR (Nujol, cm^{-1}): 1570, 1596, and 1629 ($\upsilon_{C=N}$ and $\upsilon_{C=C}$), 3251 ($\upsilon_{N\text{–}H}$) 1085 ($\upsilon_{ClO_4^-}$).

Table 2. A comparison between calculated bond lengths (Å) and angles (°) for $[NiL_{33}(MeOH)]^{2+}$ in **1** with corresponding experimental values.

		Computational level[a]					
	X-ray	6-31G* (LanL2DZ for Ni)		3-21G* (LanL2DZ for Ni)		LanL2MB	
N(1)–Ni(1)	2.097(6)	**2.115**	2.173	**2.094**	2.085	**2.098**	2.080
N(2)–Ni(1)	2.073(7)	**2.116**	2.148	**2.094**	2.056	**2.073**	2.046
N(3)–Ni(1)	2.108(7)	**2.161**	2.202	**2.118**	2.126	**2.156**	2.108
N(4)–Ni(1)	2.040(7)	**2.078**	2.142	**2.071**	1.988	**2.057**	2.023
N(5)–Ni(1)	2.061(6)	**2.140**	2.229	**2.117**	2.092	**2.104**	2.074
Ni(1)–O(1)	2.192(6)	**2.277**	2.295	**2.154**	2.129	**2.138**	2.095
N(4)–Ni(1)–N(5)	78.2(3)	**77.2**	74.9	**78.1**	79.6	**78.9**	79.7
N(4)–Ni(1)–N(2)	175.2(3)	**174.8**	173.3	**173.7**	175.1	**175.1**	175.3
N(5)–Ni(1)–N(2)	97.2(3)	**97.6**	98.8	**95.6**	95.7	**96.2**	95.7
N(4)–Ni(1)–N(1)	99.9(3)	**101.4**	105.0	**99.6**	99.0	**100.2**	99.4
N(5)–Ni(1)–N(1)	89.3(2)	**88.6**	88.3	**87.3**	87.7	**88.1**	88.0
N(2)–Ni(1)–N(1)	79.0(3)	**78.4**	76.8	**79.2**	79.5	**79.7**	80.0
N(4)–Ni(1)–N(3)	84.6(3)	**84.3**	83.2	**84.1**	85.3	**84.2**	85.0
N(5)–Ni(1)–N(3)	98.9(3)	**99.9**	100.6	**98.1**	99.1	**98.8**	99.0
N(2)–Ni(1)–N(3)	97.2(3)	**96.6**	95.8	**97.7**	96.7	**96.3**	96.2
N(1)–Ni(1)–N(3)	171.3(3)	**170.7**	169.3	**174.0**	172.5	**172.5**	172.5
N(4)–Ni(1)–O(1)	96.3(3)	**96.2**	97.6	**98.0**	95.6	**95.8**	97.3
N(5)–Ni(1)–O(1)	169.4(3)	**170.7**	168.2	**173.3**	172.2	**172.1**	172.2
N(2)–Ni(1)–O(1)	88.2(3)	**88.9**	88.9	**88.1**	89.0	**89.1**	87.3
N(1)–Ni(1)–O(1)	82.7(3)	**86.2**	84.8	**88.0**	87.0	**87.1**	85.5
N(3)–Ni(1)–O(1)	89.4(3)	**85.9**	87.4	**86.9**	86.5	**86.4**	88.0

[a] The data obtained at the HF level are given as plain text, those for the B3LYP level are in bold.

3. Results and discussion

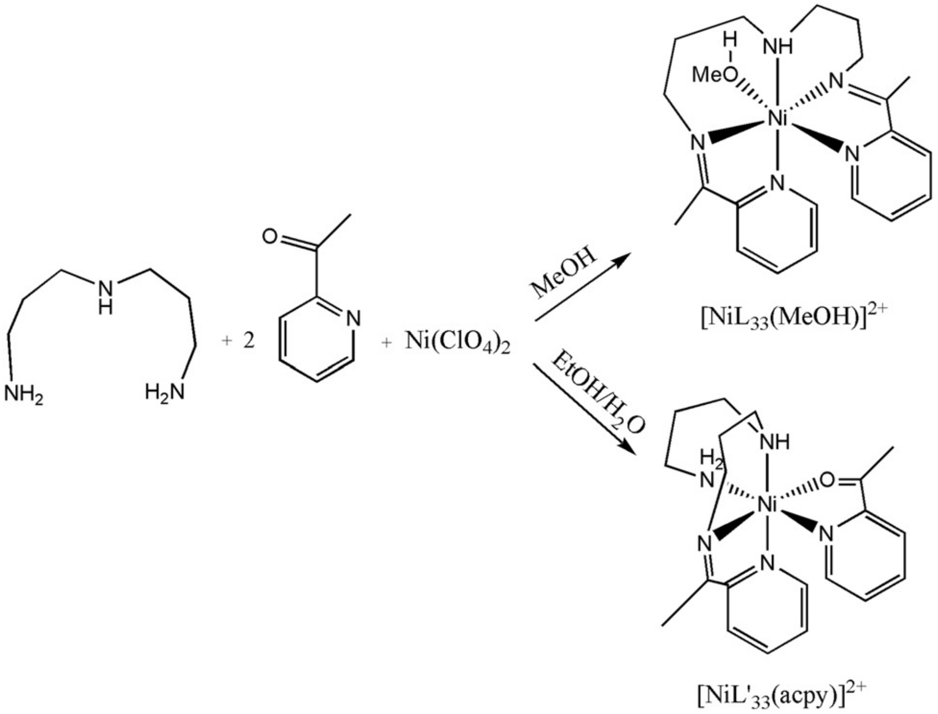
3.1. *Synthesis and characterization*

Compound **1** was prepared through full condensation of *bis*(3-aminopropyl)amine with 2-acetylpyridine in the presence of Ni(II). Condensation of both primary amino groups is confirmed by the lack of N–H stretch at 3150–3450 cm^{-1} and the presence of strong C=N (Schiff-base) stretch at 1629 cm^{-1}. The sharp band at 3251 cm^{-1} can be assigned to secondary N–H. A broad intense band at *ca* 1085 cm^{-1} due to ClO_4^- shows no splitting, indicating no coordination of ClO_4^-. The electronic spectrum in acetonitrile (10^{-6} M) shows two intense bands in the UV region, at 200–300 nm, as expected for imino-substituted pyridines [3].

3.2. *X-ray crystal structure analysis*

Crystallographic data for **1** are given in tables 1 and 2. The *R* value is quite high due to the disorder of ClO_4^- and also CH_3OH. Oxygens of ClO_4^- and oxygen and carbon of CH_3OH solvent have high-thermal parameters due to data collection at room temperature. We tried refining these atoms in two positions with reduced occupancy but while this model converged satisfactorily, there was no decrease in *R*. The quality of the crystal was also poor.

The structure with atomic numbering is shown in figure 2. Imines, pyridines, and secondary nitrogen donors as well as methanol are at apices of a distorted octahedron.



Scheme 1. The template condensation of *bis*(3-aminopropyl)amine and 2-acetylpyridine in the presence of Ni(II) in dry methanol or aqueous ethanol.

The X-ray crystal structure of a Ni(II) complex, [NiL$'_{33}$(AcPy)], derived from mono condensation of the amine and aldehyde (scheme 1), shows that in addition to the Schiff-base ligand, a molecule of 2-acetylpyridine is also coordinated [18]. In our fully condensed Schiff-base complex the angles subtended by the ligands at Ni(II) vary from 78.2(3)° to 175.3(3)°, indicating a distorted octahedral environment. The N–Ni–N bond angles in five-membered chelate rings in **1** [N(4)–Ni(1)–N(5), 78.2° and N(2)–Ni(1)–N(1), 79.0°] are close to the corresponding bond angle in [NiL$'_{33}$(AcPy)] (78.5°). The Ni–N bond lengths are in the normal range [14] from 2.041(7) to 2.193(6) Å. In [NiL$'_{33}$(AcPy)] the Ni–N$_{\text{imine}}$ bond length is equal with Ni–N$_{\text{pyridine}}$ (2.68 Å), but in **1** the Ni–N$_{\text{imine}}$ [N(2)–Ni(1), 2.072(7) and N(4)–Ni(1), 2.041(7) Å] and Ni–N$_{\text{pyridine}}$ [N(1)–Ni(1), 2.097(6) and N(5)–Ni(1), 2.060(6) Å] bond lengths are all shorter than Ni–N$_{\text{amino}}$ [(N3)–Ni(1), 2.107(7) Å].

In the packing of this complex, there are some O(coordinated CH_3OH)–H···O (perchlorate) [H1B···O6 = 2.01(6), O1···O6 = 2.85(3) Å and O1–H1B···O6 = 146(6)°] and N(amine)–H···O(perchlorate) [H3B···O3^{i} = 2.41(6), N3···O3^{i} = 3.118(15) Å and N3–H3B···O3^{i} = 151(6)°; symmetry codes: (i) (x, y, $1+z$)] hydrogen bonds.

3.3. Ab initio *and DFT studies*

For [NiL$_{33}$(MeOH)]$^{2+}$ we can consider four geometrical isomers (see figure 3, **I–IV**). In **I** and **II** the imine nitrogens occupy *trans* positions, but in **III** and **IV** they are *cis*. Isomer **I** is the isomer confirmed by X-ray crystal structure analysis. The geometry of

Table 3. Comparison of the calculated energies (E) and relative energies (ΔE) for **I** and **II**, **III**, and **IV** of $[\mathrm{NiL}_{33}(\mathrm{MeOH})]^{2+}$.

	LanL2MB		6-31G* (LanL2DZ for Ni)	
	E (Hartree)	ΔE(kcal mol^{-1})	E (Hartree)	ΔE(kcal mol^{-1})
Isomer **I**	−1322.4275250	0	−2675.8011609	0
Isomer **II**	−1322.4217195	+3.64	−2675.7875502	+8.54
Isomer **III**	−1322.4218471	+3.56	−2675.7863151	+9.32
Isomer **IV**	−1322.3998488	+17.36	−2675.76846752	+20.51

$[\mathrm{NiL}_{33}(\mathrm{MeOH})]^{2+}$ was fully optimized at both the Hartree–Fock (HF) and density functional B3LYP levels of theory. A comparison between the calculated bond lengths (Å) and bond angles (°) with corresponding experimental values is presented in table 2. Calculated bond lengths (Å) and angles (°) for **II – IV** are compared in "Supplementary material". The optimized structures of isomers **I**–**IV** are also shown in "Supplementary material". The calculated structure for **I** in the gas phase agrees well with the structure observed by X-ray crystallography. Table 3 shows the results of calculations at two different levels of theory with isomer **I** as the most stable one. Thus, it seems that the $[\mathrm{NiL}_{33}(\mathrm{MeOH})]^{2+}$ ion has adopted the most stable structure in the solid state.

4. Conclusions

We synthesized and structurally characterized a Ni(II) complex of a pentadentate Schiff base. Template condensation of *bis*(3-aminopropyl)amine and 2-acetylpyridine in dry methanol leads to fully condensed Schiff-base complex.

Supplementary material

CCDC 702952 contain the supplementary crystallographic data for **1**. This 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. Calculated bond lengths and bond angles for **II**–**IV** and optimized structures for **I**–**IV** are given also as electronic supplementary material.

Acknowledgment

The authors acknowledge the Bu-Ali Sina University for providing the necessary research facilities.

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