

Synthesis and Crystal Structure Determination of a Nickel(II) Complex of an Acyclic Pentadentate (N₅) Mono Schiff Base Ligand.

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Received: 19 June 2001; in revised form 24 September 2001 / Accepted: 22 October 2001 /

Published: 31 October 2001

Abstract: The asymmetrical tripodal tetraamine ligand N[(CH₂)₃NH₂]₂[(CH₂)₂NH₂] (ppe) was condensed with 2-acetylpyridine in the presence of nickel(II) ion. In ethanol-water solution the reaction stops after the first stage of condensation, and a new nickel(II) complex of an acyclic pentadentate (N₅) mono Schiff base ligand was obtained. X-ray structure analysis of the resulting complex, [Ni(ppe-py)(H₂O)](ClO₄)₂, indicates that condensation with 2-acetylpyridine is at the propylene chain of ppe. The geometry around the nickel ion is distorted octahedral in which the sixth co-ordination group is a solvent molecule.

Keywords: Schiff-base, Acyclic pentadentate ligand, Nickel (II) complex.

Introduction

A large number of complexes of pentadentate ligands have been reported in the literature, however, relatively few of these complexes have acyclic pentadentate (N₅) Schiff base ligands co-ordinated to the metal ion [1–5]. We have synthesised a variety of tripodal tetraamine ligands and several series of their related acyclic and macrocyclic (N₅) Schiff base complexes, using a template method [6–10].

Herein we report the synthesis of a new nickel (II) complex of an acyclic pentadentate (N_5) mono Schiff base ligand. It can be produced by the condensation of only a single primary amino group of the various aliphatic chains of the asymmetrical ligand $N[(CH_2)_3NH_2]_2[(CH_2)_2NH_2]$ (ppe) and 2-acetylpyridine.

Results and Discussion

Condensation of 2-acetylpyridine with tripodal tetraamines is a convenient and simple method of increasing the denticity of the ligand. Up to three pyridine units can be introduced by functionalising one, two or all three of the primary amine groups of the starting ligand. In the present case, where the template condensation was conducted in aqueous ethanol, the reaction stopped after a single condensation step. The formation of mono-Schiff base complex was confirmed by the elemental analysis, positive FAB-mass spectrometry and the presence of $\nu(N-H)$ as well as $\nu(C=N)$ Schiff base stretching bands in the IR spectrum. There are two $\nu(C=N)$ bands [in addition to the pyridine $\nu(C=N)$] in the IR region $1630-1671\text{ cm}^{-1}$ for Schiff base linkages. Observation of two Schiff base frequencies even after several crystallizations is more likely due to the asymmetrical nature of this complex (Figures 1 and 2). As mentioned in the following section, the X-ray crystal structure of the final product shows that condensation only occurs through the propylene chain. A broad intense band at *ca.* 1100 cm^{-1} due to ClO_4^- shows no splitting, indicating the absence of co-ordination of ClO_4^- in this complex. The electronic spectrum of the complex shows three intense bands at UV region $35,000-50,000\text{ cm}^{-1}$, as expected for imino substituted pyridines [6-9,13]. Vis. region electronic absorption data for the complex in solution is consistent with an octahedral structure, which was confirmed with X-ray crystal structure analysis.

Figure 1. Outcome of the template condensation between 2-acetylpyridine and tripodal tetraamine (ppe) in the presence of nickel(II) ion.

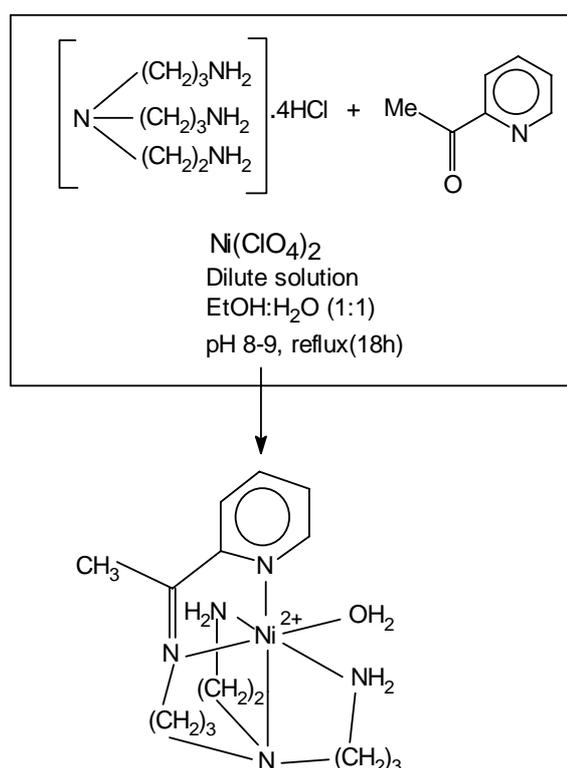
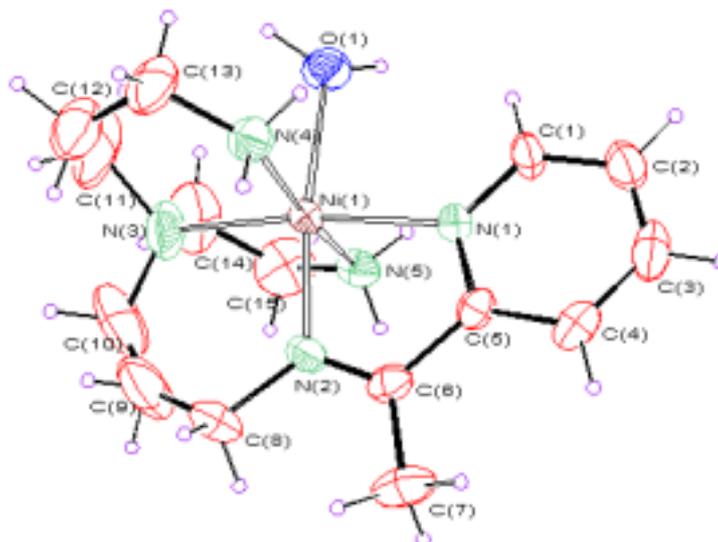


Figure 2. ORTEP plot of the complex $[\text{Ni}(\text{ppe-py})(\text{H}_2\text{O})](\text{ClO}_4)_2$. Perchlorate anions are omitted for clarity.



Description of the X-ray Structure

Crystallographic data for the $[\text{Ni}(\text{ppe-py})(\text{H}_2\text{O})](\text{ClO}_4)_2$ complex are given in Tables 1 and 2. The data reveal that the five nitrogen donor atoms of the acyclic ligands are coordinated to the metal ion in an octahedral fashion. The sixth co-ordinating group is H_2O . As can be observed from Figures 1 and 2, the tetraamine has condensed at the propylene chain. The C-N and Ni-N bond lengths are in the normal ranges (Table 2) and small distortion from regular octahedral geometry is due to the constraints of ring formation. The tertiary nitrogen of the initial tripodal tetraamine [N(3)] is *trans* to the nitrogen of the pyridine ring; a similar structure was also observed for related nickel complexes [6, 9]. The two primary amino groups of the side chains are *trans*. The crystal structure of the related nickel complex, derived from condensation reaction of tris(3-aminopropyl)amine (tpt) and acetylpyridine, $[\text{Ni}(\text{tpt-py})(\text{H}_2\text{O})](\text{ClO}_4)_2$ shows that the two aminopropyl side chains are *trans* to each other [6].

Table 1. Crystal Data and Structure Refinement for the $[\text{Ni}(\text{ppe-py})(\text{H}_2\text{O})](\text{ClO}_4)_2$

Parameter	Value	Parameter	Value
Empirical formula	$\text{C}_{15}\text{H}_{29}\text{Cl}_2\text{N}_5\text{NiO}_9$	$\rho_{\text{calcd}} (\text{g cm}^{-3})$	1.564
Formula weight	553.04	$\mu (\text{mm}^{-1})$	3.781
Temperature (K)	294(2)	$V (\text{\AA}^3)$	2349.3(8)
Wavelength (\AA)	1.54060	$F(000)$	1152
Crystal system	Monoclinic	Crystal size (mm)	0.35 X 0.30 X 0.05
Space group	$P2_1/c$	θ range ($^\circ$)	4.11 to 60.01

a (Å)	10.170(2)	Index ranges	$-6 \leq h \leq 11$
b (Å)	15.494(3)		$-17 \leq k \leq 17$
c (Å)	15.145(3)	Reflns. collected	$-16 \leq l \leq 17$
β (°)	100.119(16)		3717
Z	4	GOF on F²	1.063
		Final R(F_o²)	0.0601
		Weighted R(F_o²)	0.1643

Table 2. Selected Bond Lengths (Å) and Angles (°) for [Ni(ppe-py)(H₂O)](ClO₄)₂

Bond lengths					
M(1)-N(1)	2.093(4)	M(1)-N(4)	2.084(4)	N(2)-C(6)	1.280(7)
M(1)-N(2)	2.035(4)	M(1)-N(5)	2.099(4)	N(2)-C(8)	1.483(7)
M(1)-N(3)	2.116(6)	M(1)-O(1)	2.194(4)		
Bond angles					
N(1)-M(1)-N(2)	77.66(16)	N(2)-M(1)-N(4)	92.82(17)	N(4)-M(1)-N(5)	171.83(17)
N(1)-M(1)-N(3)	172.2(2)	N(2)-M(1)-N(5)	95.32(16)	N(4)-M(1)-O(1)	84.19(17)
N(1)-M(1)-N(4)	91.59(17)	N(2)-M(1)-O(1)	170.26(17)	N(5)-M(1)-O(1)	87.68(16)
N(1)-M(1)-N(5)	89.59(16)	N(3)-M(1)-N(4)	94.2(2)	N(2)-C(6)-C(5)	115.1(4)
N(1)-M(1)-O(1)	93.12(16)	N(3)-M(1)-N(5)	85.5(2)	N(2)-C(6)-C(7)	125.0(5)
N(2)-M(1)-N(3)	96.8(2)	N(3)-M(1)-O(1)	92.7(2)	C(6)-N(2)-C(8)	121.8(5)

Conclusions

The complex described is the result of a single Schiff base condensation of 2-acetylpyridine with a ligand containing three primary amino groups. A single product is isolated, showing that preference is given to mono-condensation over one-third conversion to the tris-condensed form. The latter reaction can be achieved in an anhydrous solvent [6,14], whereas the present reaction has been conducted in 1:1 aqueous ethanol. It is likely that the single-step limitation is simply a mass-action effect, in which the presence of a product inhibits complete reaction. Alternatively, solvation of the precursor ternary complex metal by water, which would co-ordinate more strongly than methanol, may produce a kinetic and/or steric barrier which disfavours the formation of the full tri-imine form [6, 9]. The choice of which chain undergoes condensation depends upon several factors including the electronic nature of the metal ion, the requirement of a preferred geometry of the intermediate ternary complex and pH of the reaction [6, 7, 9]. X-ray crystal structure determination has shown that in this case the tetraamine condenses at the propylene chain.

Acknowledgements

We are grateful to the Department of Chemistry of Bu Ali Sina University, Ministry of Science, Research and Technology of Iran, for the financial support.

Experimental

General

2-Acetylpyridine was obtained from Aldrich and used without further purification. The tripodal tetraamine ligand, ppe, was synthesised according to method that we have reported earlier [6,7]. IR spectra were measured on a Nicolet 5PC FT-IR instrument and UV-Vis spectra on a Shimadzu UV-265 FW spectrophotometer.

X-ray Crystal Structure Analysis.

Crystal data and the most relevant experimental parameters for the $[\text{Ni}(\text{ppe-py})(\text{H}_2\text{O})](\text{ClO}_4)_2$ complex are reported in Table 1. Single crystals were obtained by re-crystallization from water. Three-dimensional x-ray data were collected on a Rigaku AFC65 diffractometer by the ω - 2θ method, using Cu K α radiation. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least-squares regression (SHELX-97) [11]. Complex scattering factors were taken from Ref. 12 and from SHELX-97.

Synthesis of $[\text{Ni}(\text{ppe-py})(\text{H}_2\text{O})](\text{ClO}_4)_2$

This complex was readily prepared by template condensation. 2-Acetylpyridine (60 mg, 0.5 mmol, $\text{ppe}\cdot 4\text{HCl}\cdot 2.5\text{H}_2\text{O}$ (175 mg, 0.5 mmol) and $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$ (183 mg, 0.5 mmol) were refluxed for 18h in 1:1 EtOH-H₂O. The initial pH was adjusted to ca. 8–9 by addition of 5M NaOH. The solvent was removed to reduce the reaction mixture to a small volume and it was then cooled; on addition of NaClO₄, a needle-like crystalline product was obtained. Characterization of $[\text{Ni}(\text{ppe-py})(\text{H}_2\text{O})](\text{ClO}_4)_2$: Yield: 175 mg (70%); Anal. Found: C, 32.8%; H, 5.2%; N, 12.4%; C₁₅H₂₉N₅Cl₂O₉Ni requires: C, 32.6%; H, 5.2%; N, 12.7%. FAB MS (positive FAB in nitrobenzyl alcohol): m/z 434 ($(\text{M}-\text{ClO}_4)^+$, $[\text{C}_{15}\text{H}_{27}\text{N}_5\text{ClO}_4\text{Ni}]^+$, 92%) (coordinated water was also removed). IR (Nujol mull) cm⁻¹: 3447 ($\nu_{\text{O-H}}$), 3347, 3328, 3302sh, 3287 ($\nu_{\text{N-H}}$), 1665sh, 1636 ($\nu_{\text{C=N}}$, Schiff base), 1599 ($\nu_{\text{C=N}}$, py). UV-Vis. (H₂O solution) cm⁻¹: 18518sh (14.3), 12121 (10.4), 35585 (8067), 44444 (12957), where figures in parentheses are the corresponding extinction coefficients (dm³mol⁻¹cm⁻¹).

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Sample Availability: Available from the authors.

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