

Anion directed templated synthesis of mono- and di-Schiff base complexes of Ni(II)

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Received 11 March 2007; accepted 24 March 2007

Available online 30 March 2007

Abstract

Two sets of Schiff base ligands, set-1 and set-2 have been prepared by mixing the respective diamine (1,2-propanediamine or 1,3-propanediamine) and carbonyl compounds (2-acetylpyridine or pyridine-2-carboxaldehyde) in 1:1 and 1:2 ratios, respectively and employed for the synthesis of complexes with Ni(II) perchlorate and Ni(II) thiocyanate. Ni(II) perchlorate yields the complexes having general formula $[\text{NiL}_2](\text{ClO}_4)_2$ ($\text{L} = \text{L}^1$ [N^1 -(1-pyridin-2-yl-ethylidene)-propane-1,3-diamine] for complex **1**, L^2 [N^1 -pyridine-2-ylmethylene-propane-1,3-diamine] for complex **2** or L^3 [N^1 -(1-pyridine-2-yl-ethylidene)-propane-1,2-diamine] for complex **3**) in which the Schiff bases are mono-condensed terdentate whereas Ni(II) thiocyanate results in the formation of tetradentate Schiff base complexes, $[\text{NiL}](\text{SCN})_2$ ($\text{L} = \text{L}^4$ [N,N' -bis-(1-pyridine-2-yl-ethylidene)-propane-1,3-diamine] for complex **4**, L^5 [N,N' -bis(pyridine-2-ylmethylene)-propane-1,3-diamine] for complex **5** or L^6 [N,N' -bis-(1-pyridine-2-yl-ethylidene)-propane-1,2-diamine] for complex **6**) irrespective of the sets of ligands used. Formation of the complexes has been explained by anion modulation of cation templating effect. All the complexes have been characterized by elemental analyses, spectral and electrochemical results. Single crystal X-ray diffraction studies confirm the structures of four representative members, **1**, **3**, **4** and **5**; all of them have distorted octahedral geometry around Ni(II). The bis-complexes of terdentate ligands, **1** and **3** are the mer isomers and the complexes of tetradentate ligands, **4** and **5** possess trans geometry.

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Keywords: Ni(II) complexes; Tridentate schiff base; Tetradentate schiff base; Template synthesis; X-ray structure

1. Introduction

Chelating ligands play a central role in the development of the coordination chemistry related to enzymatic reaction, magnetism, molecular architectures and transition metal catalysts for oligomerization and polymerization of olefins in both academic and industrial sectors [1]. Amongst them, the enduring popularity of tridentate and tetradentate Schiff bases stems from the ease with which they can be synthesized, their versatility and their wide ranging complexing ability [2]. The tetradentate di-Schiff base ligands formed by the condensation of several diamines with salicylaldehyde or acetylacetone and their deriva-

tives are well known for many years [3]. The metal ion templated or non-templated synthesis of the mono-condensed, tridentate ligand having N_2O donor set has also been reported by several groups and the ligands have widely been used for the synthesis of homo- and heteropolynuclear complexes [4] and also as precursor for the preparation of non-symmetrical tetradentate Schiff bases [5]. On the other hand, the reports on di-Schiff bases derived from 2-pyridyl aldehydes and ketones are relatively scanty [6] and mostly stems from the interest to model the enzyme, copper–zinc superoxide dismutase (SOD) [7] and also for the synthesis of metal containing polymers with interesting optical, magnetic and electrical properties [8]. It has also been found that such tetradentate Schiff base ligands in some cases underwent hydrolytic cleavage to produce complexes of mono-condensed ligand [9]; the

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molar ratios of diamine and carbonyl compounds is not the only determining factor for mono-condensation or di-condensation of such Schiff bases. However, an explanation for such hydrolytic behaviour is still lacking.

In the present paper, we report the synthesis, structural features and spectroscopic characterization of some new complexes of Ni(II) perchlorate and Ni(II) thiocyanate with neutral mono-Schiff bases or di-Schiff bases derived from the condensation of 1,2-propanediamine or 1,3-propanediamine with pyridine-2-carboxaldehyde or 2-acetylpyridine. Here, we observe that the formation of tetradentate or tridentate ligands is directed by the counter anions. We attempt to rationalise the syntheses in the light of anion modulation of cation templating effect. Although, templated reactions are known for many years, the use of anions as templates is still a relatively young [10] and to our knowledge, there is no report where an anion directed cation templating effect has been taken into account to provide an explanation for the synthesis of complexes of tridentate and tetradentate Schiff bases.

2. Experimental

All chemicals were of reagent grade and used without further purification.

Caution!!! Although no problems were encountered in this work, perchlorate salts containing organic ligands are potentially explosive. Only a small amount of the material should be prepared and they should be handled with care.

2.1. Preparations

2.1.1. Synthesis of ligands

Two sets of ligands, set-1 and set-2 were prepared by refluxing the respective diamine (1,3-diaminopropane or 1,2-diaminopropane) (10 mmol) with 2-acetylpyridine or pyridine-2-carboxaldehyde (10 mmol for set-1 and 20 mmol for set-2) in methanol solution (20 cm³) for ca. 3 h. The ligands were not isolated. The methanol solutions were used for the syntheses of the complexes.

2.1.2. Synthesis of the complexes [Ni(L¹)](ClO₄)₂ (1) {L¹ = N¹-(1-pyridin-2-yl-ethylidene)-propane-1,3-diamine}, [Ni(L²)](ClO₄)₂ (2) {L² = N¹-pyridine-2-ylmethylene-propane-1,3-diamine} and [Ni(L³)](ClO₄)₂ (3) {L³ = N¹-(1-pyridine-2-yl-ethylidene)-propane-1,2-diamine}

To prepare complexes 1–3, a methanol solution (20 cm³) of Ni(II) perchlorate hexahydrate (5 mmol, 1.825 g) was added to the methanol solution (10 mmol) of the respective set-1 ligands (1,3-diaminopropane and 2-acetylpyridine for 1; 1,3-diaminopropane and pyridine-2-aldehyde for 2; 1,2-diaminopropane and 2-acetylpyridine for 3) and refluxed for 1 h. Orange red precipitate was separated in each case on cooling the mixture and was collected by filtration. Diffraction quality single crystals were obtained after a few days by slow evaporation of an orange acetonitrile solution

of compound 1 and 3 in open atmosphere, but all efforts to grow suitable single crystals of 2 failed.

Complex 1 (Yield: 2.14 g, 70%). *Anal. Calc.* for C₂₀H₃₀Cl₂N₆NiO₈: C, 39.25; H, 4.94; N, 13.73; Ni, 9.59. Found: C, 39.5; H, 4.8; N, 13.4; Ni, 10.8%; UV–Vis, λ_{max} (nm), (ε_{max} (dm³ mol⁻¹ cm⁻¹)) (acetonitrile), 519 (109), 795 (197). Magnetic moment, μ_{eff} = 3.1 BM.

Complex 2 (Yield: 1.99 g, 68%). *Anal. Calc.* for C₁₈H₂₆Cl₂N₆NiO₈: C, 37.02; H, 4.49; N, 14.39; Ni, 10.05. Found: C, 37.1; H, 4.6; N, 13.8; Ni, 10.6%; UV–Vis, λ_{max} (nm), (ε_{max} (dm³ mol⁻¹ cm⁻¹)) (acetonitrile), 514 (118), 795 (129). Magnetic moment, μ_{eff} = 3.2 BM.

Complex 3 (Yield: 1.68 g, 55%). *Anal. Calc.* for C₂₀H₃₀Cl₂N₆NiO₈: C, 39.25; H, 4.94; N, 13.73; Ni, 9.59. Found: C, 37.5; H, 3.8; N, 11.4; Ni, 11.6%; UV–Vis, λ_{max} (nm), (ε_{max} (dm³ mol⁻¹ cm⁻¹)) (acetonitrile), 508 (109), 797 (163). Magnetic moment, μ_{eff} = 3.1 BM.

2.1.3. Synthesis of the complexes [Ni(L⁴)](SCN)₂ (4) {L⁴ = N,N'-bis-(1-pyridine-2-yl-ethylidene)-propane-1,3-diamine}, [Ni(L⁵)](SCN)₂ (5) {L⁵ = N,N'-bis(pyridine-2-ylmethylene)-propane-1,3-diamine} and [Ni(L⁶)](SCN)₂ (6) {L⁶ = N,N'-bis-(1-pyridine-2-yl-ethylidene)-propane-1,2-diamine}

A methanol solution (20 cm³) of nickel thiocyanate tetrahydrate (10 mmol, 2.47 g) was added to the methanol solution (10 mmol) of respective set-2 ligands (1,3-diaminopropane and 2-acetylpyridine for 4; 1,3-diaminopropane and pyridine-2-aldehyde for 5; 1,2-diaminopropane and 2-acetylpyridine for 6) and refluxed for 2 h. Pale yellowish green crystals were separated in each case on cooling the mixture and were collected by filtration. Complexes 4 and 5 were re-crystallised from methanol solution to obtain needle shaped greenish yellow single crystals suitable for X-ray diffraction. No suitable single crystals could be obtained for complex 6.

Complex 4 (Yield: 2.96 g, 65%). *Anal. Calc.* for C₁₉H₂₀N₆NiS₂: C, 50.13; H, 4.43; N, 18.46; Ni, 12.89. Found: C, 50.2; H, 4.7; N, 17.9; Ni, 11.9%; UV–Vis, λ_{max} (nm), (ε_{max} (dm³ mol⁻¹ cm⁻¹)) (acetonitrile), 505 (118), 795 (129). Magnetic moment, μ_{eff} = 3.1 BM.

Complex 5 (Yield: 3.16 g, 74%). *Anal. Calc.* for C₁₇H₁₆N₆NiS₂: C, 47.8; H, 3.78; N, 19.67; Ni, 13.74. Found: C, 47.6; H, 4.1; N, 19.5; Ni, 13.9%; UV–Vis, λ_{max} (nm), (ε_{max} (dm³ mol⁻¹ cm⁻¹)) (acetonitrile), 501 (198), 872 (178). Magnetic moment, μ_{eff} = 3.1 BM.

Complex 6 (Yield: 2.50 g, 55%). *Anal. Calc.* for C₁₉H₂₀N₆NiS₂: C, 50.13; H, 4.43; N, 18.46; Ni, 12.89. Found: C, 50.2; H, 4.7; N, 18.4; Ni, 13.1%; UV–Vis, λ_{max} (nm), (ε_{max} (dm³ mol⁻¹ cm⁻¹)) (acetonitrile), 514 (164), 881 (213). Magnetic moment, μ_{eff} = 3.1 BM.

2.2. Physical measurements

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin–Elmer 240C elemental analyzer. The nickel content in all the complexes was estimated

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