Inorganica Chimica Acta 459 (2017) 103–112

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Research paper

Effect of solvents on synthesis and recrystallization of Ni(II) complex with N_2O_2-donor Schiff base

Agata Bartyzel

Department of General and Coordination Chemistry, Maria Curie-Skłodowska University, Maria Curie-Skłodowska Sq. 2, 20-031 Lublin, Poland

ARTICLE INFO

Article history:
Received 13 June 2016
Received in revised form 16 January 2017
Accepted 27 January 2017
Available online 1 February 2017

Keywords:
Chelating ligand
Nickel
Solvent effects
Crystal structure
Schiff base

ABSTRACT

The effect of different solvents on synthesis and recrystallization of Ni^{2+} complex with the tetradentate Schiff base was studied. The polar protic (MeOH and EtOH) and aprotic (ACN, DMF and THF) solvents have been used. The synthesis and recrystallization from these solvents allow obtaining seven different solvates or solvent free compounds. The products were characterized using UV–vis and FITR spectroscopy, X-ray diffraction analysis and thermogravimetry. Only in the case of DMF, the synthesis and recrystallization lead to formation of the same compound. The remaining pairs of complexes differ in their composition or/and structure. In almost all compounds the coordination environment around Ni^{2+} centre consists of two nitrogen and two oxygen atoms of Schiff bases ligand which forms the distorted square planar geometry. The compound synthesised form THF shows significant paramagnetism which suggests that the coordination geometry around metal centre is a distorted octahedral.

1. Introduction

The metal complexes with chelating ligands have been of great interest for the last few decades because they give the opportunity to obtain compounds with interesting structures and properties [1–4]. Among polydentate ligands, Schiff bases are of particular interest due to their interesting properties and potential applications in various areas such as catalysis, luminescent probes, analytical chemistry, magneto-structural chemistry, agrochemical, biological fields *etc.* [2,3,5–11]. Special attention is paid to the diimine Schiff bases having OH group in the ortho position to the amino group due to the existence of O–H···N hydrogen bond. In this type of Schiff base the keto-enol tautomerism is present. The tautomerism involves proton transfer from the hydroxylic oxygen to the imino nitrogen atom and this type of Schiff base compound often exhibits solvato-, thermo- and photochromism [9,12–14].

In this study, the effect of different solvents i.e. ethanol (EtOH), methanol (MeOH), dimethylformamide (DMF), acetonitrile (ACN) and tetrahydrofuran (THF) on synthesis and properties of nickel (II) complexes with N_2O_2-donor Schiff base (Scheme 1) was studied. Solvents are commonly used in the synthesis of ligands and their complexes. They usually play a crucial role in the synthesis and crystallisation processes of coordination compounds because different solvents lead to different crystal structures and compositions, and as a result, they affect their properties and applicability [15–19]. A number studies have shown that the solvent effect on the crystal structures is usually attributed to the following factors: (i) solubility of organic ligand in solvents; (ii) solvent size and shape; (iii) solvent polarity; (iv) protic/aprotic behaviour; (v) stoichiometric ratio of the mixed solvents [15,17,18]. Herein, the effect of solvents on the crystal structure of nickel(II) complex has been studied in two aspects: (a) solvent effect on the synthesis and (b) solvent effect on the recrystallization process. Several new species have been obtained and characterized by powder X-ray diffraction, thermal and spectroscopic (FTIR, UV–Vis) analyses. Three of them (**1b**, **2b** and **5b**) are characterized by single-crystal X-ray diffraction analysis. In the case of complexes **3b** and **4b**, despite several attempts, which have been made, on the basis of single-crystal X-ray diffraction analysis only the unit cell parameters have been determined. The solution or refinement of structures was not possible because the quality of the obtained crystal was not good; they were too small or cracked.

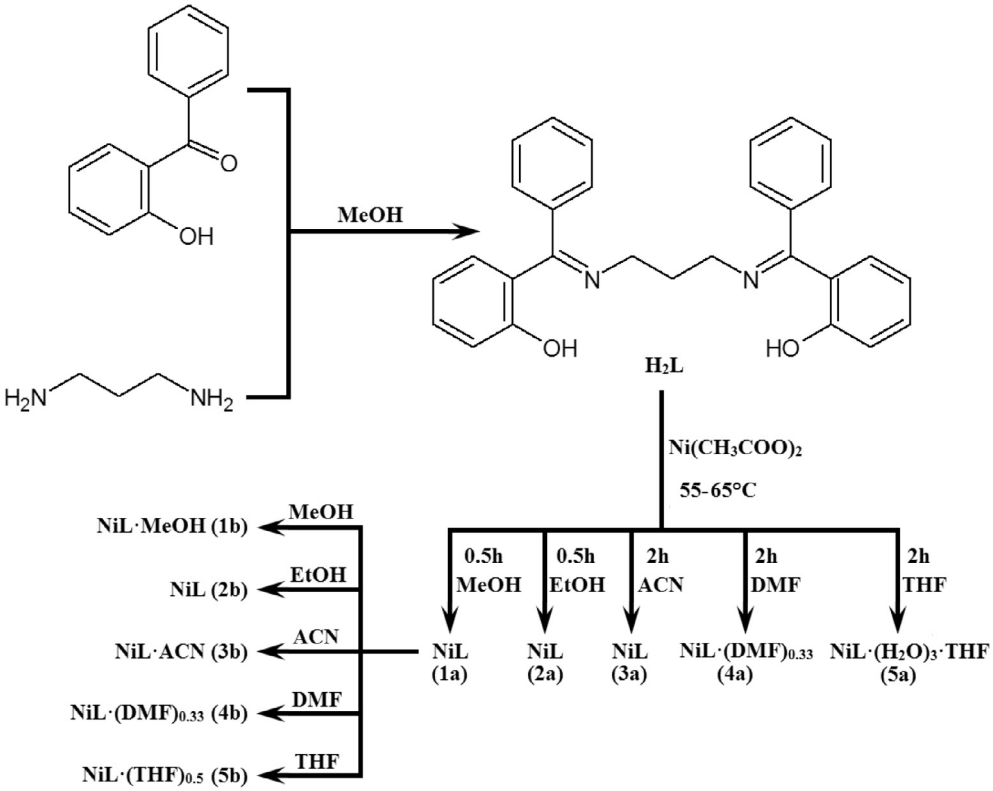
2. Experimental

2.1. Materials and preparation

1,3-Propanediamine and 2-hydroxybenzophenone (Scheme 1) used for the synthesis of Schiff base were purchased from Aldrich Chemical Company. The metal salt, $Ni(CH_3COO)_2{\cdot}4H_2O$, was bought from Alfa Aesar. The organic solvents were purchased from the Polish Chemical Reagents in Gliwice (Poland). All solvents and

E-mail addresses: adaxe13@wp.pl, agata.bartyzel@poczta.umcs.lublin.pl

http://dx.doi.org/10.1016/j.ica.2017.01.027
0020-1693/



Scheme 1. Synthetic pathway for the preparation of the nickel(II) complexes.

chemicals were reagent grade and were used without further purification. 2,2′-{(1,3-propanediyl)bis[nitrilo(phenylmethylylidene)]}diphenol (**H_2L**, where L = $C_{29}H_{24}N_2O_2$) was synthesised according to the method described in the previous paper [20].

2.1.1. *H_2L*

Yellow powder; yield: (62.0%); Elem. anal. for $C_{29}H_{26}N_2O_2$ (FW 434.53 g mol^{-1}) (%): calcd C 80.16, H 6.03, N 6.45; found C 79.96, H 5.89, N 6.26. FTIR bands (ν/cm^{-1}): 3052 (vw), 2957 (vw), 2942 (vw), 2866 (vw), 1606 (vs), 1596 (s), 1570 (s), 1495 (m), 1451 (m), 1442 (s), 1412 (m), 1330 (m), 1302 (s), 1257 (s), 1172 (w), 1152 (m), 1133 (m), 1113 (w), 1104 (w), 1073 (m), 1057 (m), 1043 (m), 1027 (m), 1014 (m), 1001 (w), 969 (w), 945 (m), 928 (m), 904 (m), 887 (w), 860 (w), 826 (m), 788 (w), 776 (m), 762 (s), 756 (vs), 715 (vs), 703 (s), 687 (s). UV–vis [2.5·10^{-5} mol L^{-1}, λ_{max}/nm (ε x 10^4/L mol^{-1} cm^{-1})]: in MeOH: 212 (3.59), 257 (1.90), 282 (0.82)sh, 321 (0.64), 401 (0.36); in EtOH: 230 (2.29), 258 (2.06), 284 (0.73)sh, 321 (0.72), 403 (0.31); in ACN: 210 (5.09), 257 (2.13), 321 (0.88), 404 (0.08)sh; in DMF: 267 (1.66), 322 (0.88), 405 (0.06)sh; in THF: 212 (4.79), 259 (2.09), 325 (0.95). ^{1}H NMR (δ, $CDCl_3$): 1.98–2.03 (quint, 2H, >CH_2), 3.36–3.40 (t, 4H, 2× >CH_2), 6.61–6.64 (ddd, 2H, ArH), 6.75–6.79 (dd, 2H, ArH), 6.92–6.97 (dd, 2H, ArH), 7.10–7.13 (m, 4H, ArH), 7.25–7.28 (ddd, 2H, ArH), 7.41–7.47 (m, 6H, ArH), 15.61 (s, 2H, 2×OH).

2.2. Synthesis of complexes ***1a–5a***

In the case of studying the solvent effects on the synthesis, all compounds were prepared in a similar way. The Schiff base ligand (0.61 mmol) was dissolved in 25 mL of appropriate solvent at 55–65 °C. Next, hot solution of nickel(II) acetate (0.61 mmol in 20 mL) was added dropwise to the solution of ligand. The reaction mixtures were refluxed for 30–120 min. The complexes **1a** and **2a** were filtered off as soon as the polycrystalline products were precipitated. The remaining complexes **3a–5a** were isolated after reduction of solvents volume to 15 ml. The precipitates were collected by filtration, washed several times with appropriate solvents and dried in air atmosphere.

2.2.1. NiL (***1a***)

Light brown needles; yield: (69.6%); Elem. anal. for $C_{29}H_{24}N_2O_2$-Ni (FW 491.21 g mol^{-1}) (%): calcd C 70.91, H 4.92, N 5.70; found C 70.81, H 4.89, N 5.84. FTIR bands (ν/cm^{-1}): 3077 (vw), 3054 (vw), 3021 (vw), 2981 (vw), 2928 (vw), 2874 (vw), 2859 (vw), 1598 (s), 1586 (m), 1571 (s), 1528 (s), 1489 (w), 1457 (s), 1436 (vs), 1347 (s), 1340 (vs), 1277 (w), 1264 (s), 1249 (s), 1217 (w), 1175 (m), 1145 (s), 1120 (m), 1089 (w), 1071 (m), 1029 (m), 1000 (w), 968 (w), 956 (m), 943 (m), 930 (w), 912 (m), 881 (w), 845 (s), 817 (vw), 779 (m), 769 (m), 757 (vs), 747 (vs), 724 (m), 701 (vs), 687 (s), 669 (m), 661 (m). UV–vis [2.5·10^{-5} mol L^{-1} MeOH solution, λ_{max}/nm ($\varepsilon \times 10^4$/L mol^{-1} cm^{-1})]: 209 (5.54), 241 (3.94), 265 (4.95), 348 (0.85), 412 (0.50).

2.2.2. NiL (***2a***)

Yellow-orange needles; yield: (67.1%); Elem. anal. for $C_{29}H_{24}N_2O_2Ni$ (FW 491.21 g mol^{-1}) (%): calcd C 70.91, H 4.92, N 5.70; found C 70.56, H 4.84, N 5.68. FTIR bands (ν/cm^{-1}): 3054 (vw), 3019 (vw), 2926 (vw), 2858 (vw), 1598 (s), 1587 (m), 1570 (s), 1527 (s), 1490 (w), 1457 (s), 1436 (vs), 1347 (s), 1340 (vs), 1277 (w), 1263 (m), 1249 (s), 1217 (w), 1175 (m), 1145 (s), 1121 (m), 1089 (w), 1071 (m), 1030 (m), 1001 (w), 956 (m), 944 (m), 929 (w), 912 (m), 882 (w), 845 (s), 802 (w), 779 (m), 757 (vs), 747 (vs), 725 (m), 701 (vs), 687 (s). UV–vis [2.5·10^{-5} M EtOH solution, λ_{max}/nm ($\varepsilon \times 10^4$/L mol^{-1} cm^{-1})]: 203 (5.82), 236 (4.11), 261 (5.04), 346 (0.86), 413 (0.52).