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Fluorous schiff base ligands and their nickel(II) complexes: synthesis, characterization and solubility properties in supercritical CO₂

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ABSTRACT

New supercritical carbon dioxide soluble ligands, (E)-2-((3-(trifluoromethyl) phenyl imino)methyl)phenol, (E)-2-((4-(trifluoromethyl)phenylimino) methyl)phenol, (E)-2-methoxy-6-((3-(trifluoromethyl)phenylimino)methyl) phenol, (E)-2-methoxy-6-((4-(trifluoromethyl) phenylimino)methyl)phenol and their nickel(II) complexes have been prepared and characterized by spectroscopic methods and elemental analysis. The solubility of the synthesized compounds was measured at 343.15K and 172.4 bar in supercritical carbon dioxide. © 2008 Trade Science Inc. - INDIA

KEYWORDS

Schiff base;
Chelate;
Metal extraction;
Supercritical carbon dioxide.

INTRODUCTION

During the past decades, there has been a great deal of interest in the synthesis and characterization of transition metal Schiff base complexes because of exceptional stability and unique electronic properties^[1,2]. These complexes find a number of applications; in particular, they have been used as reagents in analytical chemistry, biochemistry, spectrophotometric analysis and aqueous-phase extraction of metal ions^[3,4].

Chelating combined with solvent extraction is one of the most widely used techniques for preconcentration and separation of metal ions from aqueous samples for analytical purposes^[5]. In many cases, conventional solvent extraction requires use of toxic organic liquids, generating environmental problems for handling and disposal of used solvents^[6]. Supercritical fluid extraction (SFE) has become a viable alternative to conventional solvent extraction for the recovery of organic compounds from environmental and biological samples^[7].

Carbon dioxide is commonly employed in supercritical fluid processing since it is readily available in large quantities, inexpensive and non-flammable. Furthermore, it has a low critical temperature, moderate critical pressure, low viscosity and few toxicity dangers. Despite these numerous advantages, there are many potential applications that are not viable for CO₂ due to equilibrium limitation^[6]. For example heavy metals, polar compounds and commercially available surfactants and chelating agents exhibit little, if any, solubility in supercritical carbon dioxide. The reported studies indicate that fluorination of chelating agent results in dramatic enhancement of solubility^[4-6]. Hence the later studies concentrated on identifying or synthesizing supercritical carbon dioxide (ScCO₂) soluble chelating agent.

The present paper reports the synthesis, characterization of fluorinated Schiff base derivatives ligands and their nickel(II) complexes. The structures of the synthesized compounds have been identified with spec-

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trosopic methods such as FT IR, ¹H NMR, and elemental analysis. This paper also involves measurement of solubility of synthesized ligands and complexes in scCO₂. The solubility of the synthesized compounds was measured using by high pressure reactor at 343.15 K and 172.4 bar in scCO₂.

EXPERIMENTAL

All chemicals were of reagent grade quality and used further purifications. (E)-2-((phenylimino)methyl)phenol (HL) and its nickel(II) complex[Ni(L)₂] were prepared according to the literature and used for compare with the synthesized fluorus ligands and complexes solubility^[2]. The ¹H NMR spectra were obtained on a Bruker-Advance DPX 400 spectrometer in CDCl₃. IR spectra were recorded on a Perkin Elmer Mattson 1000 FT-IR spectrometer as KBr pellets in range 4000-400cm⁻¹. Elemental analyses were recorded on a LECO CHNS-932 analyzer and Hitachi 180-80 polarized zeeman atomic absorption spectrometer. Melting point was determined on a Gallenkamp apparatus in a sealed capillary and is uncorrected. CO₂ with a purity of 99.99% was supplied by BOSS Company (Adana, Turkey). The solubility of studies were performed with stainless steel batch reactor (PARR, 50 ml, windowed) and syringe pump (ISCO, series D) in sc CO₂.

General procedure for preparation of ligands

For preparation of ligands an ethanol solution 3 or 4-trifluoromethylaminobenzene (2.0 mmol) was added drop wise, at room temperature, to a solution of 2-hydroxybenzaldehyde or 2-hydroxy-3-methoxybenzaldehyde(2mmol) in 30mL ethanol, yielding a large amount of yellow precipitate. The mixture was stirred for 30min at room temperature and filtered under vacuum. Crystallization from dichloromethane gave the spectroscopically pure product as yellow crystalline compound.

(E)-2-((3-(trifluoromethyl)phenylimino)methyl)phenol (HL¹)

0.49g in 92.5 % yield, mp. 221-223°C. Anal. Calcd for C₁₄H₁₀F₃NO: C, 63.40; H, 3.80; N, 5.28. Found: C, 63.24; H, 3.91; N, 5.02 %. ¹H NMR(TMS), δppm: 13.41(br s, 1H, OH), 8.26(s, 1H, CH=N), 7.82-

[Ni(L²)₂]: 0.42g in 71.52% yield. Anal. Calcd for C₂₈H₁₈F₆N₂NiO₂: C, 57.28; H, 3.09; N, 4.77; Ni, 10.00. Found: C, 56.88; H, 3.12; N, 4.47; Ni, 9.29%. FT-IR(KBr) vcm⁻¹: 1598 (C=N), 1521, 1442(Ar-H), 1291(C-ONi), 469(Ni-N), 435(Ni-O).

[Ni(L³)₂]: 0.47g in 72.6 % yield. Anal. Calcd for C₃₀H₂₂F₆N₂NiO₄: C, 55.67; H, 3.43; N, 4.33; Ni, 9.07. Found: C, 56.03; H, 3.51; N, 4.59; Ni, 8.65 %. FT-IR (KBr) vcm⁻¹: 2981, 2896(C-H), 1589(C=N), 1522, 1464(Ar-H), 1317(C-ONi), 477(Ni-N), 423(Ni-O).

[Ni(L⁴)₂]: 0.49g in 75.7 % yield. mp. Anal. Calcd for C₃₀H₂₂F₆N₂NiO₄: C, 55.67; H, 3.43; N, 4.33; Ni, 9.07. Found: C, 55.33; H, 3.54; N, 4.19; Ni, 8.77 %. FT-IR(KBr) vcm⁻¹: 2976, 2911 (C-H), 1592(C=N), 1507, 1451(Ar-H), 1307(C-ONi), 471(Ni-N), 419(Ni-O).

General procedure for solubility measurements in sc CO₂

The solubility of the synthesized Schiff base and their nickel(II) complexes were measured qualitatively in scCO₂ as described below. The reactor(50mL, windowed) was placed on a stir-plate, agitated by a magnetic stir bar and temperature was controlled with water bath. In a typical experiment, a 100-150mg of appropriate ligands or metal complex sample and magnetic stirrer were loaded into the glass tube (2.5×2.0cm I.D.). The glass tube was sealed with a black band filter paper, weighed (±0.1 mg) and inserted into the stainless steel vessel. The reactor was then partially charged with CO₂, brought to the operating temperature and CO₂ pressure adjusted until the desired pressure and statically extracted for 45min. After pressure was reduced, the tube(with filter paper and magnetic stirrer) weighted and solubility calculated as mmol L⁻¹ (TABLE 1).

RESULTS & DISCUSSION

The main focus of this work is the design and synthesizing of new scCO₂ soluble ligands. For this aim, fluorinated derivative of well known Schiff base ligands and their nickel(II) complexes(M/L=1/2) have been synthesized and determined of solubility in scCO₂. General procedure for preparation of ligands(HL¹-HL⁴) and their nickel(II) complexes is shown in SCHEME 1. Analytical and spectroscopic data for the synthesized compounds are given in experimental section.

7.43(m, 8H, phenyl). FT-IR(KBr) vcm^{-1} : 3380(OH), 1628(C=N), 1521, 1447(Ar-H), 1279(C-OH).

(E)-2-((3-(trifluoromethyl)phenylimino)methyl)phenol (HL²)

0.47g in 88.61 % yield, mp. 197-199°C. Anal. Calcd for $\text{C}_{14}\text{H}_{10}\text{F}_3\text{NO}$: C, 63.40; H, 3.80; N, 5.28. Found: C, 63.32; H, 3.87; N, 5.12 %. ¹H NMR(TMS), δ ppm: 13.02(br s, 1H, OH), 8.59 (s, 1H, CH=N), 7.63-7.09 (m, 8H, phenyl). FT-IR (KBr) vcm^{-1} : 3372(OH), 1630 (C=N), 1512, 1451 (Ar-H) 1266(C-OH).

(E)-2-methoxy-6-((3-(trifluoromethyl)phenylimino)methyl)phenol (HL³)

0.44g in 74.5 % yield, mp. 237-239°C. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{F}_3\text{NO}_2$: C, 61.02; H, 4.10; N, 4.74. Found: C, 60.68; H, 4.18; N, 4.61 %. ¹H NMR(TMS), δ ppm: 13.75(br s, 1H, OH), 8.42 (s, 1H, CH=N), 7.78-7.22 (m, 8H, phenyl). FT-IR (KBr) vcm^{-1} : 3378(O-H), 2971, 2966(C-H), 1620 (C=N), 1508, 1464(Ar-H), 1282(C-OH).

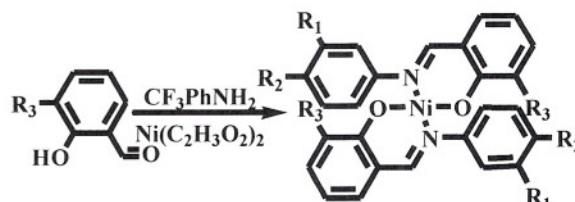
(E)-2-methoxy-6-((4-(trifluoromethyl)phenylimino)methyl)phenol (HL⁴)

0.51g in 86.4 % yield, mp. 221-224°C. Anal. Calcd for $\text{C}_{15}\text{H}_{12}\text{F}_3\text{NO}_2$: C, 61.02; H, 4.10; N, 4.74. Found: C, 60.57; H, 4.21; N, 4.56 %. ¹H NMR(TMS), δ ppm: 13.28(br s, 1H, OH), 8.38(s, 1H, CH=N), 7.65-7.18 (m, 8H, phenyl). FT-IR(KBr) vcm^{-1} : 3352(O-H), 2978, 2972(CH₃), 1624(C=N), 1501, 1453(Ar-H), 1271(C-OH).

General procedure for preparation of complexes

For preparation of complexes a solution of 0.25g, (1mmol) $\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ in 20mL Et-OH was added to a solution of the corresponding ligands (2mmol) in 35mL EtOH at room temperature. The reaction mixture was stirred for 2h, at 80°C to get an orange-red solution. The mixture was concentrated to 20mL to precipitate out of complexes from the solution as dark red solid. The crude product was recrystallized from warm dichloromethane.

[Ni(L¹)₂]: 0.37g in 63.0% yield. Anal. Calcd for $\text{C}_{28}\text{H}_{18}\text{F}_6\text{N}_2\text{NiO}_2$: C, 57.28; H, 3.09; N, 4.77; Ni, 10.00. Found: C, 56.45; H, 3.17; N, 4.33; Ni, 9.78 %. FT-IR(KBr), cm^{-1} : 1602(-HC=N), 1535, 1451(Ar-H), 1311(C-ONi), 475(Ni-N), 425(Ni-O).



SCHEME 1

	HL ¹ , Ni(L ¹) ₂	HL ² , Ni(L ²) ₂	HL ³ , Ni(L ³) ₂	HL ⁴ , Ni(L ⁴) ₂
R ¹	CF ₃	H	CF ₃	H
R ²	H	CF ₃	H	CF ₃
R ³	H	H	OCH ₃	OCH ₃

Characterization

The elemental analysis data of the synthesized ligands and their nickel(II) complexes are in agreement with the theoretical values. The ¹H NMR spectra of ligands(HL¹-HL⁴) showed singled peaks at δ =13.41, 13.02, 13.75 and 13.28 ppm respectively, that assigned as OH protons. The azomethine proton of ligands were observed in agreement with the literature data, at δ =8.26, 8.59, 8.42 and 8.38 ppm respectively^[1,3,9].

The IR spectra of the Schiff base ligands were compared with nickel complexes to obtain the information about the binding the ligand to nickel in the complexes. The characteristic strong band of the azomethine(-HC=N) group were observed at 1630-1620 cm^{-1} in the spectra of free ligands. It is expected that coordination of the nitrogen to the metal atom would reduce the electron density in the azomethine group and thus lower the -HC=N absorption^[9]. This band is shifted to the region 1602-1589 cm^{-1} region in the nickel complexes indicating the azomethine-nickel coordination^[1,9]. The spectra of free ligand show strong band in the 1282-1266 cm^{-1} , assigned to the C-O stretching of the phenol group. However, after complexation these bands observed at 1317-1291 cm^{-1} indicating the other coordination of the Schiff bases through the phenolic oxygen atom.

Solubility measurements

The solubility of the ligands and their nickel(II) complexes were determined using the method as given in the experimental section. The solubility data of the synthesized compounds are given in terms of mmol of sample in a liter of CO₂(TABLE 1). It has been observed from the result of the solubility studies that, the

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TABLE 1 : Solubility of ligands and complexes in scCO₂ at 343.15K and 172.4 bar

Compound	MW	Solubility	
		mg/L	(mol/L)
HL	197.2	94	4.76×10 ⁻⁴
HL ¹	265.2	220	8.29×10 ⁻⁴
HL ²	265.2	180	6.78×10 ⁻⁴
HL ³	295.3	340	1,15×10 ⁻³
HL ⁴	295.3	280	9.48×10 ⁻⁴
[Ni(L) ₂]	451.2	-	*
[Ni(L ¹) ₂]	587.2	36	6.13×10 ⁻⁵
[Ni(L ²) ₂]	587.2	48	8.17×10 ⁻⁵
[Ni(L ³) ₂]	647.1	90	1.39×10 ⁻⁴
[Ni(L ⁴) ₂]	647.1	78	1.21×10 ⁻⁴

*Lower than 1×10⁻⁵

fluorinated Schiff base ligands have shown better solubility in scCO₂ in comparison the non-fluorinated ligands.

These results parallel finding of enhanced solubility of other fluorinated ligands.^[4-7] On the other hand, solubility of metal complexes in scCO₂ is important factor in determining the efficiency of metal extraction using. Careful inspection of the solubility data obtained indicated that, the nickel(II) complexes of the ligands are much more stable in scCO₂ than free ligands. From the result of this work, it may be concluded that fluorinated Schiff base ligands and their nickel(II) complexes shows more solubility than non-fluorinated derivative, therefore may potentially be used in metal extraction as a chelating agent in scCO₂.

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