

SYNTHESIS OF CO₂- SOLUBLE SHIFF BASE TYPE CHELATING AGENT FOR SUPERCRITICAL EXTRACTION OF HEAVY METALS

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Fluorination of the alkyl groups include metal chelating agents solubilities have increase in scCO₂. In this study, two new shiff base type ligands *N*-[3,5-bis(trifluoromethyl) benzene] salisildimin, *N*-(3,5-bistrifluoromethyl phenyl)-2-hydroxy-5-methoxy benzal dimine, that they substituted CO₂-philic groups as trifluoroalkyl were synthesized. Cu(II), Fe(III) complexes of the synthesized ligands were prepared and structures of the the ligands and the complexes have been characterized by elemental analysis, UV-vis, IR, ¹H NMR and single crystal X-ray spectroscopy. Feasibility of extracting some heavy metal ions from water with the synthesized ligands were investigated by conventional methods.

INTRODUCTION

Supercritical fluid extraction has become a viable alternative to conventional solvent extraction for the recovery of organic compounds from environmental and biological samples [1]. Carbon dioxide is commonly employed in supercritical fluid processing because it is readily available in large quantities, inexpensive and non-flammable. Further, it has a low critical temperature, moderate critical pressure, low viscosity and few toxicity dangers. Despite these numerous advantages, there are many potential application that are not viable for CO₂ due to equilibrium limitation For example heavy metals, polar compounds and commercially available surfactants and chelating agents exhibit little, if any, solubility in CO₂. Although many investigators have employed this problem. Studys shown that fluorination of the alkyl groups include metal chelating agents solubilities have increase in scCO₂ [2,3].

Shiff bases are well known as effective chelating agents for a broad range of transition metal ions. In this paper, synthesis of fluorinated shiff bases and their metal complexes is reported. The new chelating agents were applied in the solvent extraction of Cu(II) and Fe(III) ions from aqueous solution at different pH (3-5), extraction time (1, 3, 6, 10, 20, 30 min.) and different metal chelate ratio (M/L: 1/2, 1/4, 1/8). Metal extraction ratio is determined using atomic absorption and Uv-visible spectroscopy

I. MATERIALS AND METHODS

General

The shiff base and their metal complexes were prepared according to literatures methods [4, 5, 6]. All chemical were of reagent grade quality and used further purification. NMR spectras were recorded on a Bruker-Avance DPX 400 spectrometer. Elemental analyses were recorded on a CHNS-932 (LECO) analyser and Hitachi 180-80 polarized Zeeman

Atomic Absorption spectrometer. Extraction data were obtained as mean values after at least three test under each set of experimental conditions. In all cases the standard deviations were less than 4%.

***N*-[3,5-bis(trifluoromethyl) phenyl]salisildimine (HL¹)(C₁₅H₉NF₆O):** A solution of 3,5-bis(trifluoromethyl) aniline (0.02 mol, 4.7 g) in EtOH (50 mL) was added to solution of salicylaldehyde (0.02 mol 2.44 g) at 55-60 °C. The color of the solution turned to yellow. The reaction was stirred for 2 h, and after that cooled, yellow-orange precipitated was filtered under room temperature and recrystallized from CHCl₃ (Figure 1). The yield of the brown solid product was 72.8 % m.p. 96 °C ; ¹H NMR (ppm, in CDCl₃) 12.25 s (1H, -OH), 8.5 s (1H, -HC=N-), 7.6-6.9 m (7H, Ph) ; I.R.(KBr pellets, cm⁻¹): 3454 (-OH), 3000 (C-H, Ar), 1600 (C-H, Ph), 1570 (-CH=N-); UV-vis (max abs.) : 346nm, e : 7340 ; Elementel analyses Calc. for (%) : C, 54.06 ; H, 2.72 ; N, 4.20 Found for (%) : C, 54.18 ; H, 2.23 ; N, 4.23; single crystal x-ray spectrum; crystal system: monoklinik, volume (A³):1395,3 (3), crystal size (mm): 0.3x0.3x0.02, plate yellow and the selected geometric parameters given at Table 1

Table 1. Selected geometric parameters for HL¹ **Table 2.** Selected geometric parameters for HL²

Bond Leight (A°)	Bond Angles (°)
N1-C8 : 1.417(4)	C9-C8-N1 : 123.6 (3)
N1-C7 : 1.276(4)	C7-N1-C8 : 119.5 (3)
C6-C7 : 1.439(4)	N1-C7-C6 : 123.5 (3)
O1-C5 : 1.360(4)	C5-C6-C7 : 120.6 (3)
C1-C6 : 1.381(4)	O1-C5-C6 : 122.0 (3)
C8-C9 : 1.377(4)	C5-O1-H1 : 109.5

Bond Leight (A°)	Bond Angles(°)
N1-C9 : 1.412(4)	C4-C2-C8 : 116.6 (3)
N1-C7 : 1.280(4)	C7-N1-C9 : 118.9 (3)
C6-C7 : 1.442(4)	N1-C7-C6 : 123.2 (3)
O1-C5 : 1.352(4)	C5-C6-C7 : 121.6 (3)
O2-C8 : 1.430(4)	O1-C5-C6 : 122.4 (3)
C1-C6 : 1.397(5)	C5-O1-H1 : 109.49
C5-C6 : 1.389(4)	O2-C4-C5 : 115.6 (3)

***N*-(3,5-Bis(trifluoromethyl) phenyl)-2-hydroksi-5-methoxy benzaldimine Synthesis (HL²)**

(C₁₆H₁₁NF₆O₂): A solution of 3,5-bis(trifluoromethyl)aniline (0.02 mol 4.7 g) in EtOH (50 mL) was added dropwise to a solution of o-vaniline (0.02 mol 3.16g) in 25 mL of EtOH at 55-60 °C The color of the solution turned to orange. The reaction was stirred for 2 h, and after that cooled, yellow-orange precipitated was filtered under room temperature. The product was recrystallized from CHCl₃ (Figure 2). The yield of the orange solid product was 64 % m.p. 121 °C; ¹H NMR(ppm, in CDCl₃): 12.5 s (1H, -OH), 8.5 s (1H, -HC=N-), 6.6-7.7 m (6H, Ph) 3.8 s (-OCH₃,H); I.R.(KBr pellets, cm⁻¹): 3454 (-OH), 3068 (C-H, Ar), 1600 (C-H, Ph), 1570 (-CH=N-); UV-vis (max abs.) : 303, e : 28660 ; Elementel analyses Calc. for (%) : C, 52.90 ; H, 3.05 ; N, 3.85 Found for (%) : C, 53.06 ; H, 2.62 ; N, 3.88; single crystal x-ray spectrum; Crystal System : monoklinik, volume (A³) :1491,0(5), crystal size(mm): 0.2x 0.2x0.01, plate yellow and the selected geometric parameters given at Table 2.

***bis* (N-[3,5-bis(trifluoromethyl)benzene] salisildiminato) Copper (II) Complexes**

(C₃₀H₁₆N₂F₁₂O₂Cu): A solution of Cu(CH₃COO)₂.H₂O (0.25 mmol 0.05 g) in EtOH (25 mL) was added to a solution of the HL¹ (0.5 mmol 0.173 g) in EtOH (25 mL) at pH 5 that the reaction medium pH was adjustable with buffer solution. After the mixture was refluxed for 3 h while heating at 55-60 °C, brown precipitate was filtered and dried in vacuo and than

recrystallized from chloroform. The yield was 54.8 %, m.p. 273°C I.R. (KBr pellets, cm^{-1}) : 3058 (C-H,Ar), 1530 ($-\text{CH}=\text{N}-$); UV-vis (max abs.): 391, ϵ : 16614 and paramagnetic.

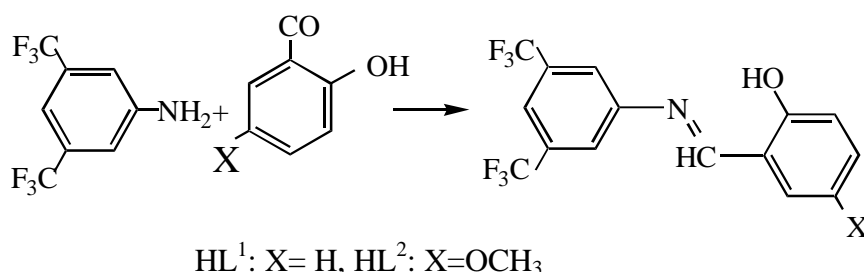
tris(N-(3,5-Bis(trifluoromethyl) phenyl -2-hydroxy-5-methoxybenzaldiminato) Ferric (III) Complexes ($\text{C}_{32}\text{H}_{20}\text{N}_2\text{F}_{12}\text{O}_4\text{Fe}$): A solution of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.068 mmol 0.027 g) in EtOH (25 mL) was added to a solution of the HL^2 (0.137 mmol 0.05 g) in EtOH (25 mL) at pH 5. After the mixture was refluxed for 5 h while heating at 45-50 °C, red-brown precipitate was filtered and dried in vacuo and then recrystallized from chloroform. The yield was 71.4 %, m.p. 71°C, I.R. (KBr pellets, cm^{-1}): 1640(C-H,Ph), 1561($-\text{CH}=\text{N}-$)UV-vis (max abs.): 310, ϵ : 23403 and paramagnetic.

Using This Ligands at Metal Extraction: All the Schiff bases investigated were capable of effecting extraction of transition metal Cu(II) into the organic solvent studies. This ligand extraction effects was investigated at different pH (3-5), extraction time (1, 3, 6, 10, 20, 30 min) and metal chelate ratio (M/L:1/2, 1/4, 1/8).

Aqueous solution containing 4×10^{-4} M $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ in appropriate buffer were equilibrated with appropriate volumes of chloroform solution of Schiff bases HL^1 (4×10^{-4} M) by shaking in a mechanical shaker at 40 °C at specific time. After phase separation the absorbans of organic phase was measured. The extraction efficiency was calculated on the basis of the determination of the Cu(II) content in organic phases by UV-vis spectrophotometry and aqueous phases by atomic absorption spectrometry. Some results of extraction shown at Figure 3.

CONCLUSION

General method of synthesis is given in Scheme 1. Analytical and spectroscopic data can be found in detail in material and method section.



Scheme 1. Synthesis reaction of ligands

The results of the elemental analysis of the synthesized Schiff base and their metal complexes are in agreement with the theoretical values. All the peaks obtained by ^1H NMR spectra for all ligands and metal complexes were consistent with the literature [4,5,7]. The structures of ligands were determined by X-ray crystallography for crystals grown from CHCl_3 . ORTEP drawing of HL^1 and HL^2 are shown Figure 1 and 2 respectively [8].

Of the synthesised ligands, HL^1 was the most effective extractand of Cu (II) and Fe (III) from aqueous solutions reaching 94,27 % extraction of the Cu (II) ion, under metal-ligand ratio: 1/4, pH: 3 and 20 min extraction period (figure 3).

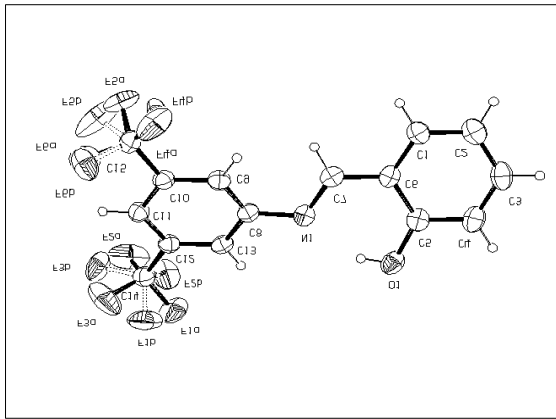


Figure 1. ORTEP drawing of HL¹

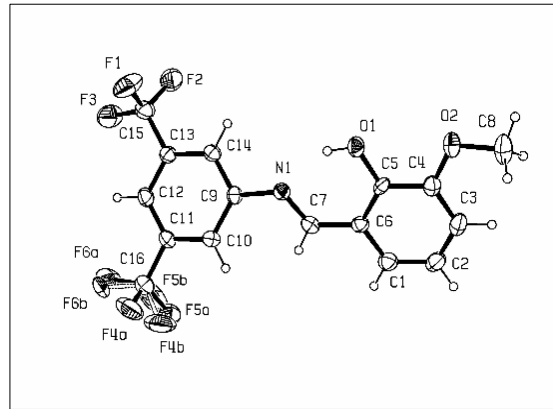


Figure 2. ORTEP drawing of HL²

On the other hand, HL² ligand were shown extracted only Fe(III) ions.

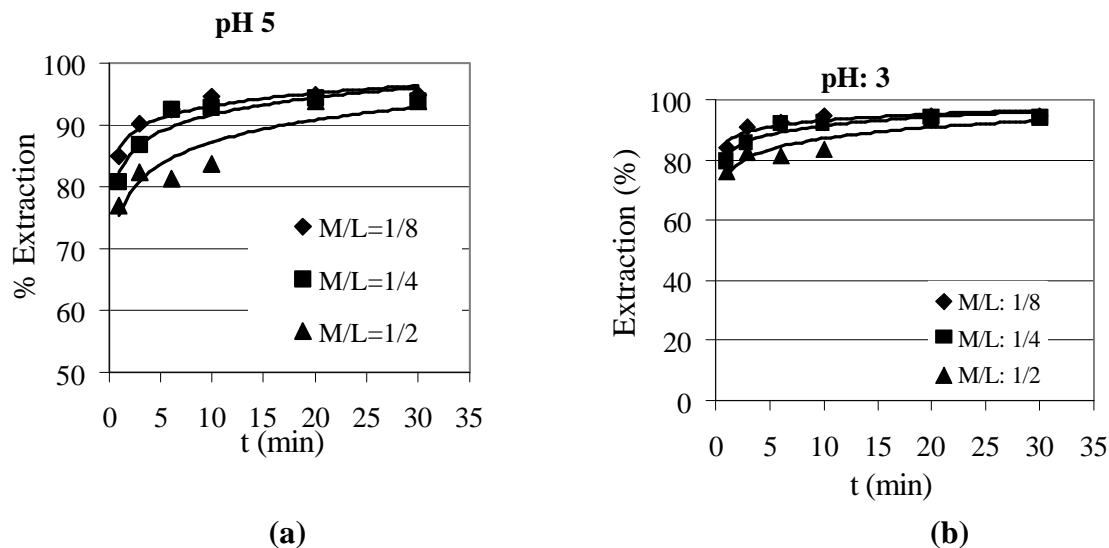


Figure 3: Extraction efficiency of HL1 for Cu(II) at pH: 3 (a) and pH: 5 (b)

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