

Synthesis and Characterization of New Extractants for Cu(II)

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New extractants for Cu²⁺ ions in raw ore powders or waste water (fluid) were successfully synthesized recently in good yields. Their structures and purity were confirmed by ¹H NMR and IR.

Key Words: Extractant, Cu(II), Synthesized, Oximatio, Hydrazone formation.

INTRODUCTION

Copper, as one of the most important metals, is widely used in many fields such as copper fitting, heat exchanger tube sheet, electric cable, lead wire, transformer, switch, printed circuit board, vacuum pump, bullet, cannonball, pipe, pipe fitting, copper also has a biological action at low. However, more than 34 % of the copper mined is now in landfill, 18 % of the copper mined was lost as tailings and other wastes during milling and smelting¹. Although pyrometallurgical treatment of complex metal sources containing copper is frequently used in practice, it is not suitable or economically viable when it is used in the field of multi component metal alloys and other complex materials with multi components.

Solvent extraction technology offers a convenient method for the extraction and separation of copper(II) from complex mixtures as mentioned above and can be efficiently applied for the selectively recovery of copper from leach liquors and other waste solutions or fluids, so solvent extraction is becoming increasingly important in the production of copper from nature raw ores or other sources or solid waste recently, which are suited to the processing of wastes such as slags², tailings³, post-flotation waste and mine waters⁴.

Although some of the reagents of this category, namely LIX26⁵, LIX64N⁶, LIX622N⁷, LIX 84-I⁷, LIX984⁸ and Acorga M5640⁹, offer strong extraction of copper from acidic media, many problems still remain unsolved. For example, they have low exchange capacity for the ion exchange and the low durability and unsatisfactory selectivity of the electrodialysis membrane.

In order to develop new extraction agents with high exchange capacity, strong durability, high selectivity and

suitable to low pH system, we have successfully synthesized six new extractants recently in our laboratory and evaluate their structures on the basis of their IR and ¹H NMR.

EXPERIMENTAL

Preparation of 5-tert-butyl-2-hydroxybenzaldehyde (A)¹⁰: Magnesium turnings (28.8 g, 1.2 mol) were added to anhydrous methanol (535 mL) to form an 8 % w/w methanol solution of magnesium methoxide. Toluene (160 mL) and the solution of magnesium methoxide were stirred and refluxed until all the magnesium was dissolved and H₂ evolution ceased. 4-tert-butylphenol (300 g, 2 mol) was added and refluxed for 1 h. Toluene (330 mL) was added and the mixture was distilled under vacuum to remove the methanol-toluene azeotrope. Paraformaldehyde (117.6 g) in toluene (200 mL) was added slowly with concurrent removal of solvent by distillation. After cooling to room temperature, H₂SO₄ (10 %, 800 mL) was added slowly with stirring and heated to 50 °C to dissolve all solids. The product was extracted with toluene (3 × 100 mL), washed with water (3 × 200 mL), dried over MgSO₄, concentrated *in vacuo* and purified by column chromatography (eluting) to yield a yellow oil (260.2 g, 73.1 %).

Preparation of (B): A solution of the hydroxylamine hydrochloride (22.24 g, 0.32 mol) neutralized by NaHCO₃ in H₂O (50 mL) was slowly added to A (53.4 g, 0.3 mol) in ethanol (100 mL). The resulting mixture was stirred for 4 h under reflux and the solvent was removed *in vacuo* to yield a white solid which needs no further purification (50.2 g, 86.7 %).

Preparation of (C): A solution of A (53.4 g, 0.3 mol) in ethanol (100 mL) was slowly added to methyl hydrazine (0.33 mol) in ethanol (50 mL). The resulting mixture was stirred for 4 h under reflux and the solvent was removed *in vacuo* to

yield a yellow solid which needs no further purification (59.6 g, 96.4 %).

Preparation of 3-bromo-5-*tert*-butyl-2-hydroxybenzaldehyde (D): Bromine (29.1 g, 0.185 mol) in glacial acetic acid (500 mL) was added to a solution of (A) (31.2 g, 0.177 mol) and NaOAc·3H₂O (41 g, 0.35 mol) in glacial acetic acid (100 mL) *via* a dropping funnel over 4 h at 60 °C. The yellow solution was stirred for another 2 h. The solvent was removed *in vacuo*. The solid was washed with Na₂S₂O₅ solution (300 mL, 10 % w/w), saturated NaHCO₃ solution (400 mL) and petroleum ether (100 mL) to give yellow crystals (35.9 g, 88.6 %).

Preparation of (E): A solution of the hydroxylamine hydrochloride (10.48 g, 0.152 mol) neutralized by NaHCO₃ in H₂O (60 mL) was slowly added to (D) (38.4 g, 0.15 mol) in ethanol (100 mL). The resulting mixture was stirred for 4 h under reflux and the solvent was removed *in vacuo* to yield a white solid which needs no further purification (36.5 g, 86.6 %).

Preparation of (F): A solution of (E) (38.4 g, 0.15 mol) in ethanol (100 mL) was slowly added to methylhydrazine (0.16 mol) in ethanol (50 mL). The resulting mixture was stirred for 4 h under reflux and the solvent was removed *in vacuo* to yield a yellow solid which needs no further purification (41.9 g, 98.3 %).

Preparation of 5-*tert*-butyl-2-hydroxy-3-methoxybenzaldehyde (G): NaOCH₃ (129.6 g, 2.4 mol) and CuBr (17 g) was dissolved in the minimum anhydrous methanol (100 mL), (D) (102.4 g, 0.4 mol) was dissolved in DMF (250 mL) and poured into the refluxing mixture of the NaOCH₃/MeOH solution. The resulting solution was refluxed 6 h. After the solution was cooled to room temperature, 2500 mL H₂O was added to the solution, air pump filtration, the solid was washed with H₂O and petroleum ether to yield a yellow solid (44.9 g, 53.9 %).

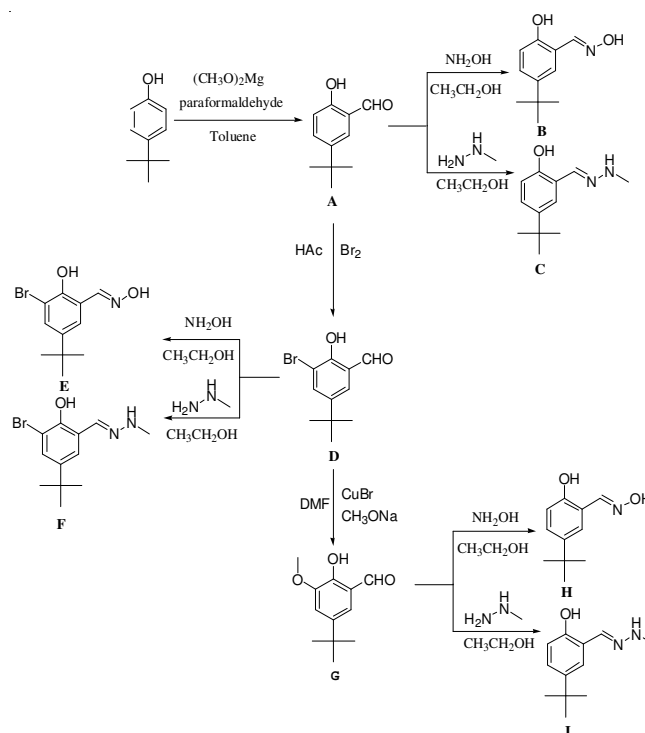
Preparation of (H): A solution of the hydroxylamine hydrochloride (0.33 g, 0.01 mol) neutralized by NaHCO₃ in ethanol (10 mL) was slowly added to G (2.08 g, 0.01 mol) in ethanol (20 mL). The resulting mixture was stirred for 4 h under reflux and the solvent was removed *in vacuo* to yield a yellow solid which needs no further purification (1.89 g, 91.7 %).

Preparation of (I): A solution of G (2.08 g, 0.01 mol) in ethanol (10 mL) was slowly added to methylhydrazine (0.01 mol) in ethanol (10 mL). The resulting mixture was stirred for 4 h under reflux and the solvent was removed *in vacuo* to yield a yellow solid which needs no further purification (2.16 g, 97 %).

RESULTS AND DISCUSSION

Six new extrantants were synthesized from *p-tert*-butylphenol, as shown in **Schemes-I**: (1) Synthesis of 5-*tert*-butyl-2-hydroxybenzaldehyde (A)¹⁰, the reaction involves magnesium mediated *ortho*-formylation. (2) Synthesis of brominating salicylaldehydes (D), bromine in glacial acetic acid was added to the solution of (A) and sodium acetate in glacial acetic acid *via* a dropping funnel. (3) Methoxylation: the reaction in this work was carried out by adding (D) in DMF into a refluxing mixture of a fresh 4 M NaOMe/MeOH solution, CuBr under nitrogen. (4) Oximation: (B)¹¹, (E), (H) were synthesized by adding hydroxylamine to aldehydes. (5) Hydrazone Formation: (C), (F), (I) were synthesized by slowly adding the appropriate salicylaldehyde precursors to hydrazines.

All the compound we have synthesized in our lab were confirmed by ¹H NMR and IR (Table-1).



Schemes-I: Reaction pathway to (C), (D), (E) (F), (G) and (I)

TABLE-1
CHARACTERIZATION DATA OF THE INTERMEDIATES A, B, D AND E AS WELL AS OF THE C-SUBSTITUTED PENTAMETHINE CYANINE DYES C, F AND G

Compound	IR (ν_{\max} cm ⁻¹)	¹ H-NMR(CDCl ₃)
A		1.35 [s, 9H, C(CH ₃) ₃], 6.92-7.33 (m, 3H, Ar-H) 9.87 (s, 1H, CHO), 10.80 (s, 1H, OH)
B	3359 (PhOH) 2966 (C-H) 1623 (C=N)	1.25 [s, 9H, C(CH ₃) ₃], 4.01 (s, 2H, OH) 6.92-7.33 (m, 3H, Ar-H), 8.38 (s, 1H, CH=N) 10.71 (s, 1H, OH)
C	3392 (PhOH) 2957 (C-H) 1623 (C=N)	1.34 [s, 9H, C(CH ₃) ₃], 2.09 (s, 1H, -NH-C) 3.00 (d, 3H, N-CH ₃), 6.91-7.24 (m, 3H, Ar-H) 8.39 (s, 1H, CH=N), 11.21 (s, 1H, OH)
D	3356 (PhOH) 2960 (C-H) 1689 (CHO)	1.35 [s, 9H, C(CH ₃) ₃], 7.52-7.82 (m, 2H, 2Ar-H) 9.87 (s, 1H, CHO), 10.44 (s, 1H, OH)
E	3170 (PhOH) 2970 (C-H) 1623 (C=N)	1.25 [s, 9H, C(CH ₃) ₃], 7.48 (d, 1H, Ar-H), 7.51 (d, 1H, Ar-H), 8.15 (s, 1H, CH=N), 10.70 (s, 1H, OH), 11.70 (s, 1H, OH)
F	3347 (PhOH) 2950 (C-H) 1623 (C=N)	1.25 [s, 9H, C(CH ₃) ₃], 2.09 (s, 1H, -NH-C) 2.82 (s, 3H, N-CH ₃), 7.07-7.43 (d, 2H, Ar-H), 8.15 (s, 1H, CH=N), 11.44 (s, 1H, OH)
G	3355 (PhOH) 2971 (C-H) 1689 (CHO)	1.34 [s, 9H, C(CH ₃) ₃], 3.82 (s, 3H, OCH ₃) 7.15-7.22 (2H, 2Ar-H), 9.92 (s, 1H, CHO) 10.65 (s, 1H, OH)
H	3378 (PhOH) 2967 (C-H) 1623 (C=N)	1.25 [s, 9H, C(CH ₃) ₃], 3.85 (s, 3H, OCH ₃) 6.78 (d, 1H, Ar-H), 6.85 (d, 1H, Ar-H), 8.16 (s, 1H, CH=N), 10.70 (s, 1H, OH), 11.70 (s, 1H, OH)
I	3362 (PhOH) 2971 (C-H) 1623 (C=N)	1.26 [s, 9H, C(CH ₃) ₃], 2.09 (s, 1H, -NH-C) 2.92 (s, 3H, N-CH ₃), 3.85 (s, 3H, OCH ₃) 6.76-6.89 (d, 2H, Ar-H), 8.15 (s, 1H, CH=N), 11.21 (s, 1H, OH)

Conclusion

Six extractants were synthesized in good yields. The structure and purity of the prepared compounds were confirmed by ^1H NMR and IR.

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