SYNTHESIS OF COPPER(II), NICKEL(II), ZINC(II) AND MANGANESE(II) COMPLEXES MIXED LIGAND FROM SULFONAMIDES OF ANTHRANILIC ACID AND 2-, 3-, 4-AMINOPYRIDINES

A THESIS

BY

SUTANUN DOUNGSOONGNUEN

Presented in Partial Fulfillment of the Requirements for the

Master of Science Degree in Chemistry

at Srinakharinwirot University

May 2011

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AN ABSTRACT

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Sutanun Doungsoongnuen. (2011). *Synthesis of copper(II), nickel(II), zinc(II) and manganese(II) complexes mixed ligand from sulfonamides of anthranilic acid and 2-, 3-, 4-aminopyridines*. Master thesis, M.S. (Chemistry). Bangkok: Graduate School, Srinakharinwirot University. Advisor Committee: Assoc. Prof. Dr. Supaluk Prachayasittikul, Dr.Ratchanok Pingaew.

This study describes the synthesis of metals; copper(II), nickel(II), zinc(II) and manganese(II) complexes (**L1-M-L2**) derived from mixed ligands of sulfonamides (**L1**) and 2-, 3-, 4- aminopyridines (**L2**) and metal (**M**) salts. The synthesis was performed using the ligands (**L1** and **L2**) and metal salts in the ratio of 1 : 1 : 1 mmol. The sulfonamide derivatives (**L1**) have been synthesized by sulfonylation of anthranilic acid using *p*-substituted benzenesulfonyl chlorides in water, instead of organic solvents, which is a friendly environmental condition. The synthetic sulfonamides were purified by column chromatography. The structures of sulfonamides metal complexes were analyzed using IR spectra and magnetic moment.

การสังเคราะห์สารโลหะเชิงซ้อนคอปเปอร์ นิกเกิล สังกะสี และแมงกานีส ลิแกนด์ผสม ซัลโฟนาไมด์ของกรดแอนทรานิลิกและ 2-, 3-, 4-อะมิโนพิริดีน

บทคัดย่อ

ของ

สุตนันท์ ดวงสูงเนิน

เสนอต่อบัณฑิตวิทยาลัย มหาวิทยาลัยศรีนครินทรวิโรฒ เพื่อเป็นส่วนหนึ่งของการศึกษา
ตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต สาขาวิชาเคมี
พฤษภาคม 2554

สุตนันท์ ดวงสูงเนิน. (2554). *การสังเคราะห์สารโลหะเชิงซ้อนคอปเปอร์ นิกเกิล สังกะสี และแมงกานีส ลิแกนด์ผสมซัลโฟนาไมด์ของกรดแอนทรานิลิกและ 2-, 3-, 4-อะมิโนพิริดีน*. ปริญญานิพนธ์ วท.ม. (เคมี). กรุงเทพฯ: บัณฑิตวิทยาลัย มหาวิทยาลัยศรีนครินทรวิโรฒ. คณะกรรมการควบคุม: รองศาสตราจารย์ ดร.สุภาลักษณ์ ปรัชชญาสิทธิกุล, ดร.รัชนก ปิ่นแก้ว

การศึกษานี้ได้สังเคราะห์สารโลหะเชิงซ้อนคอปเปอร์ นิกเกิล สังกะสี และแมงกานีส (**L1**-**M**-**L2**) โดยใช้ลิแกนด์ผสมอนุพันธ์ซัลโฟนาไมด์ (**L1**) และ 2-, 3-, 4-อะมิโนพิริดีน (**L2**) และเกลือของโลหะ (**M**) ดังกล่าว ทำปฏิกิริยาในอัตราส่วน 1 : 1 : 1 mmol โดยอนุพันธ์ซัลโฟนาไมด์ (**L1**) นั้นสังเคราะห์ได้จากปฏิกิริยา sulfonylation ของกรดแอนทรานิลิก และ *p*-substituted benzene-sulfonyl chloride ทั้งนี้การสังเคราะห์อนุพันธ์ซัลโฟนาไมด์นั้นเป็นปฏิกิริยาในสภาวะที่เป็นมิตรต่อสิ่งแวดล้อม เนื่องจากใช้น้ำเป็นตัวทำละลายแทนการใช้ตัวทำละลายอินทรีย์ อนุพันธ์ซัลโฟนาไมด์ที่สังเคราะห์ได้ ทำให้บริสุทธิ์โดยแยกด้วยคอลัมน์โครมาโทกราฟี และพิสูจน์โครงสร้างโดยใช้ข้อมูลทางสเปกโทรสโกปี สำหรับสารโลหะเชิงซ้อนของอนุพันธ์ซัลโฟนาไมด์วิเคราะห์โครงสร้างโดยใช้ข้อมูล FT-IR และ magnetic moment

The thesis titled

"Synthesis of copper(II), nickel(II), zinc(II) and manganese(II) complexes mixed ligand from sulfonamides of anthranilic acid and 2-, 3-, 4-aminopyridines"

by

Sutanun Doungsoongnuen

has been approved by the Graduate School as partial fulfillment of the requirements for the Master of Science Degree in Chemistry of Srinakharinwirot University.

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Acknowledgements

I would like to express my most sincere gratitude to my supervisor, Associate Professor Dr.Supaluk Prachayasittikul, for her kindness, invaluable guidance, helpful supervision and her hearty encouragement throughout this work.

I am grateful to Dr.Ratchanok Pingaew, my co-advisor, for her endless kindness, thoughtful advice, valuable time, patient reading and warm encouragement. In addition, I am grateful to Dr.Thammaruk Suksrichavalit, Center of Data Mining and Biomedical Informatics, Faculty of Medical Technology, Mahidol University and Dr.Patcharin Chaisuwan for their useful comments and encouragements.

I gratefully acknowledge financial support from Professor Dr.Virapong Prachayasittikul, Department of Clinical Microbiology and Applied Technology, Faculty of Medical Technology, Mahidol University.

I wish to express my appreciation to all of my teachers of the Department of Chemistry, Faculty of Science, Srinakharinwirot University for their helps, teaching and discussion during I was a student here. Also, I am grateful to graduate students of the Department of Chemistry, Faculty of Science, Srinakharinwirot University for their encouragement, generosity and helpfulness. Particularly, special thanks are extend to Mr. Payung Jiarawapi for recording the nuclear magnetic resonance spectra. I would like to thank the staffs of the Department of Chemistry, Faculty of Science, Srinakharinwirot University for their friendship, kind support and encouragement.

Finally, this work was eventually successful with understanding, great love, supports and encouragements from my parents and family.

Sutanun Doungsoongnuen

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CHAPTER 1

INTRODUCTION

Background

Sulfonamides (**1**) are amides of sulfanilic (**2**) or sulfonic acid (**3**), commonly known as sulfa drugs. They show anti-growth activity against microorganisms and have been used for treatment and prevention of infectious diseases. Sulfonamides are classified as anti-metabolite or the chemical which is structurally similar to metabolite required for life. There are various kinds of sulfonamide drugs that have been used, for examples, sulfisoxazole (**4**) sulfamethoxazole (**5**) sulfadiazine (**6**) sulfadoxazine (**7**) sulfapyridine (**8**) and sulfacetamide (**9**) (Patrick. 2005: 382-387). Their structures are illustrated in Figure 1.

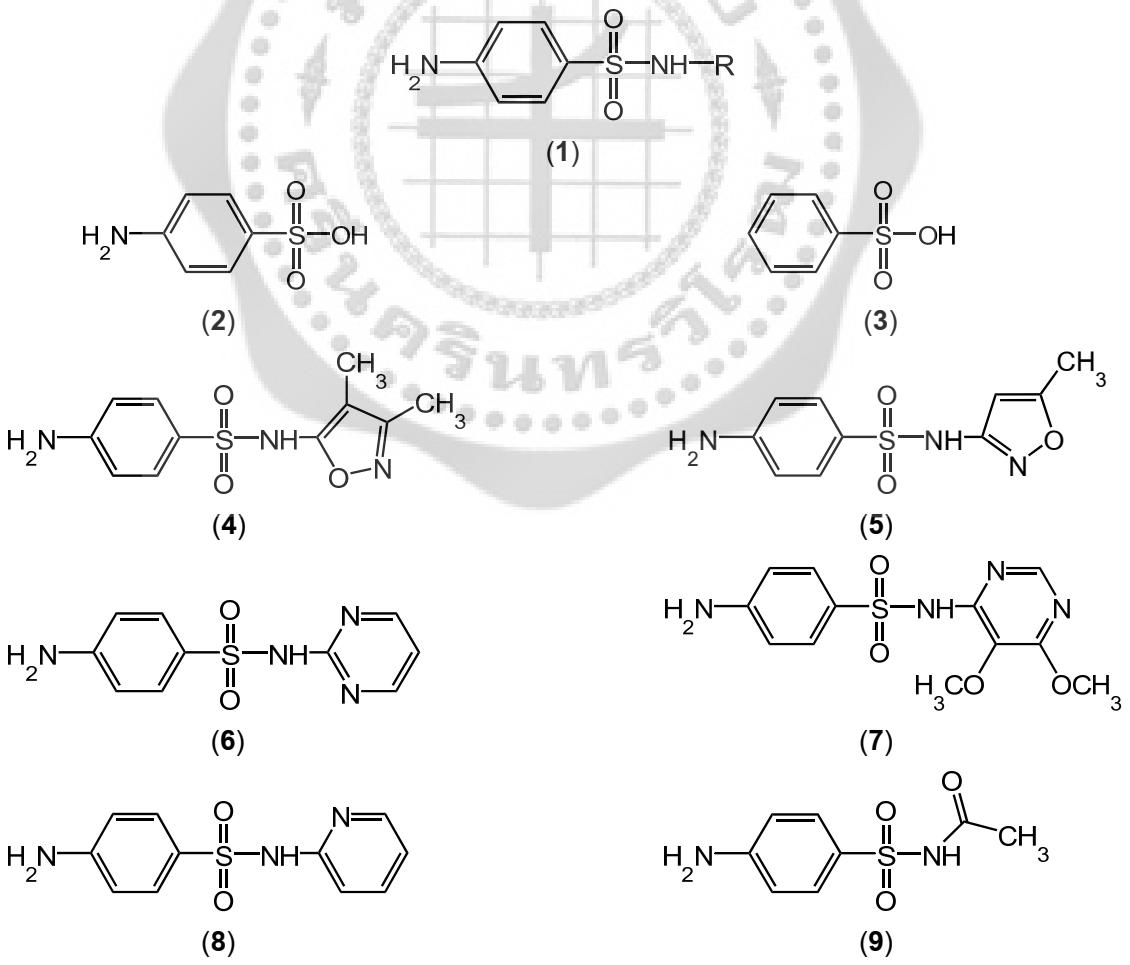


Figure 1 Chemical structures of sulfonamides **1, 4-9**

Sulfonamides have a similar structure to *p*-aminobenzoic acid (**10**, Fig.2) which is an intermediate in the synthesis of tetrahydrofolate in bacteria. It has been shown that the sulfonamide group (-SO_2NH-R) of sulfa drugs is essential for pharmacological actions and antibacterial activity (**10**).

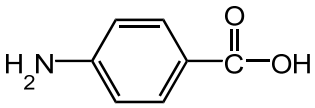
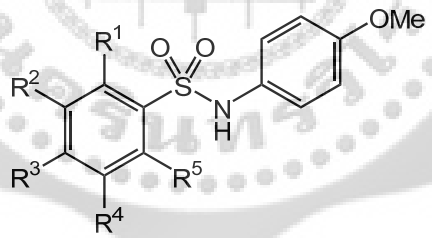


Figure 2 Structure of *p*-aminobenzoic acid (**10**)

Moreover, a number of sulfonamide derivatives with interesting biological activities have been reported such as halogenated sulfonamides (**11**) which inhibit the growth of cancer cells MCF-7/ADR on drug resistance or multidrug resistant (Medina; et al. 1999: 1843-1846), indole-3-sulfonamides (**12**) which are potent HIV non-nucleoside reverse transcriptase inhibitors (NNRTIs) (Zhao; et al. 2008: 554-559), coumarin 3-(*N*-aryl) sulfonamides (**13**) which are anti-cancer (Reddy; et al. 2004: 4093-4097), and *bis*-sulfonamide (**14**) which are antibacterials (Wilkinson; et al. 2007: 1355-1357). The structures of **11**-**14** are shown in Figures 3-6.



(**11**)

R^1	R^2	R^3	R^4	R^5	R^1	R^2	R^3	R^4	R^5
Br	F	F	F	F	F	F	H	F	F
F	Br	F	F	F	H	F	F	F	H
F	F	Br	F	F	H	H	F	F	F
F	F	Cl	F	H	F	H	F	H	F
H	F	F	F	F	F	Cl	F	Cl	F
F	H	F	F	F	F	F	F	F	F

Figure 3 Chemical structure of halogenated sulfonamide (**11**)

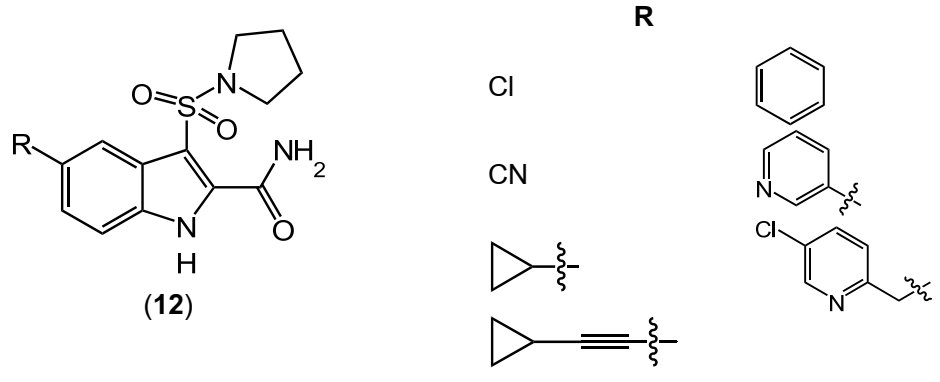
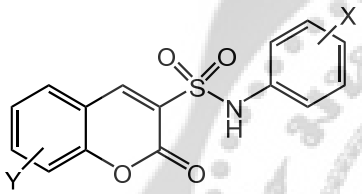


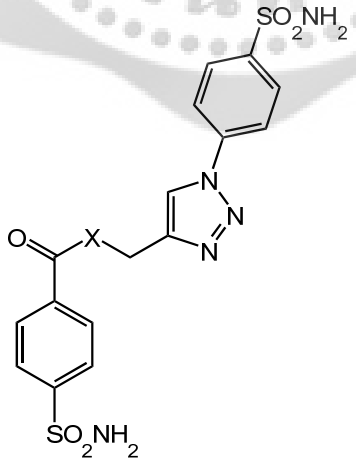
Figure 4 Chemical structures of indole-3-sulfonamides (**12**)



(**13**)

X	Y	X	Y
4-OMe	8-Br	4-F, 3-NH_2	6-OMe
4-OMe	6-Cl	4-Br	6-OMe
4-OMe	8-OEt	4-Br	8-OEt
4-OMe, 3-OH	6-Cl	4-Br	8-Cl
4-F, 3-NH_2	8-OEt	4-Br	8-Br

Figure 5 Structures of coumarin 3-(*N*-aryl) sulfonamides (**13**)

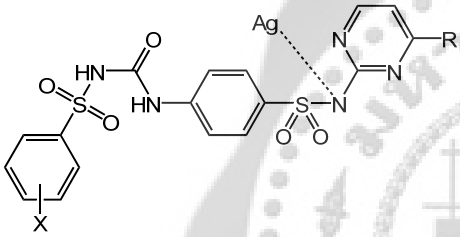


(**X** = O, NH)

(**14**)

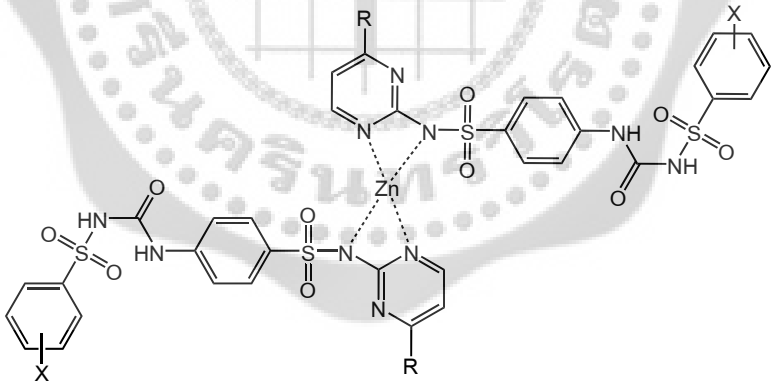
Figure 6 Structures of *bis*-sulfonamides (**14**)

According to the interesting features of bioactivities of sulfonamide derivatives, the synthesis of sulfonamide metal complex derivatives has been reported. Examples are silver(I) and zinc(II) complex of sulfa drug derivatives as arylsulfonylureido group (**15**, **16**) which display antifungal action (Mastrolorenzo; Scozzafava; & Supuran. 2000: 99-107), nickel(II) and cobalt(II) complexes of methanesulfonic acid hydrazide (**17**) with antibacterial activity against gram positive bacteria (*Staphylococcus aureus*, *Bacillus subtilis* and *Bacillus magaterium*) and gram negative bacteria (*Salmonella enteritidis* and *Escherichia coli*) (Özdemir; et al. 2009: 2613-2618). Moreover, copper(II) complex (**18**) derived from mixed ligands; 2,6-pyridine-dicarboxylic acid and 2-aminopyridine was reported to exhibit antibacterial and antifungal actions (Yenikaya; et al. 2009: 3526-3532). The structures of metal complexes **15**-**18** are summarized in Figures 7-9.



(**15**)

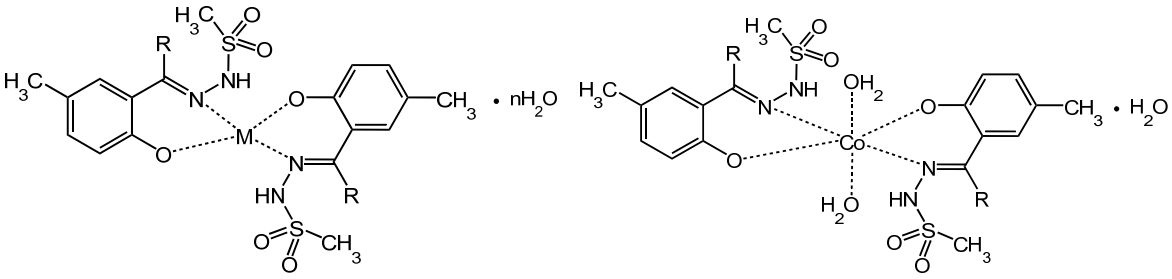
(**15a**); **X** = H, R = H
(**15b**); **X** = 4-F, R = H
(**15c**); **X** = 4-Cl, R = H
(**15d**); **X** = 4-Me, R = H
(**15e**); **X** = 2-Me, R = H
(**15f**); **X** = H, R = Me
(**15g**); **X** = 4-F, R = Me
(**15h**); **X** = 4-Cl, R = Me
(**15i**); **X** = 4-Me, R = Me
(**15j**); **X** = 2-Me, R = Me



(**16**)

(**16a**); **X** = H, R = H
(**16b**); **X** = 4-F, R = H
(**16c**); **X** = 4-Cl, R = H
(**16d**); **X** = 4-Me, R = H
(**16e**); **X** = 2-Me, R = H
(**16f**); **X** = H, R = Me
(**16g**); **X** = 4-F, R = Me
(**16h**); **X** = 4-Cl, R = Me
(**16i**); **X** = 4-Me, R = Me
(**16j**); **X** = 2-Me, R = Me

Figure 7 Silver(I) complex (**15**) and zinc(II) complex of sulfonamides (**16**)



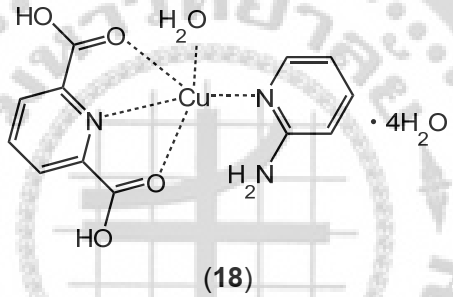
(**17**) (**17d**); **R** = CH_3

(**17a**); **R** = H, M = Ni, n = 2

(**17b**); **R** = H, M = Co, n = 2

(**17c**); **R** = CH_3, M = Ni, n = 0

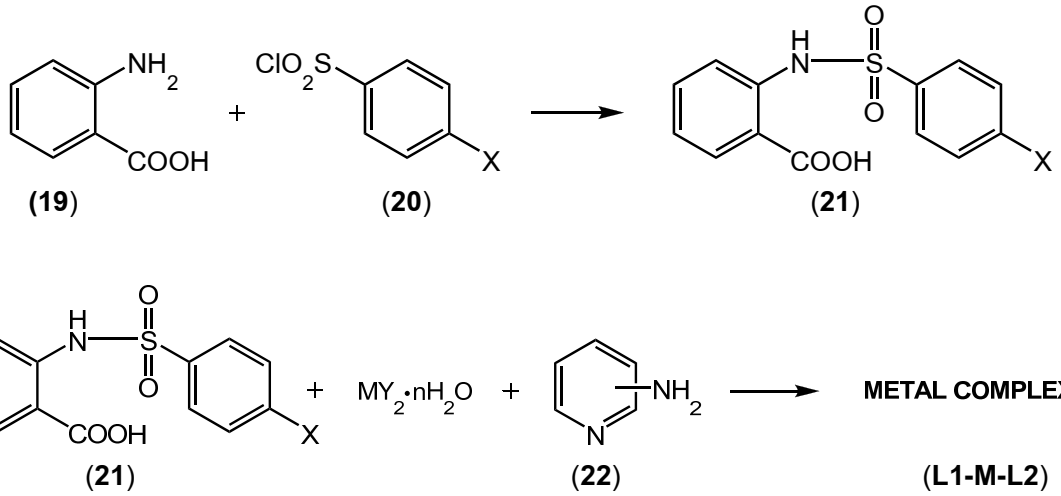
Figure 8 Structures of nickel(II) complex and cobalt(II) complex (**17**)



(**18**)

Figure 9 Structures of copper(II) mixed ligand complex (**18**)

Based on the reported bioactivities of sulfonamide metal complexes deriving mostly from sulfanilamide (sulfa drug), thus, other ligands for the synthesis of new metal complexes have been focused. Therefore, the synthesized of sulfonamide derivatives of anthranilic acid are selected as the ligands. This study aims to synthesize mixed ligands; anthranilic acid sulfonamides (**21** denoted as **L1**) and 2-, 3-, 4-aminopyridines (**22** denoted as **L2**) metal complexes represented as **L1**-**M**-**L2**. The sulfonamide derivatives (**21**) were achieved from the reaction of anthranilic acid (**19**) and arenesulfonyl chlorides (**20**) as shown in Scheme 1. The expected metal complexes **L1**-**M**-**L2** were synthesized as shown in Scheme 1.



X = NO_2, OCH_3, CH_3, Cl

M = Cu(II), Zn(II), Ni(II), Mn(II)

Y = CH_3COO, Cl

Scheme 1 Synthesis of sulfonamide (**21**) and their metal complexs

Aminopyridines possess *N*,*N*-electron donors thus, they were used as ligands (Scheme 1) for this study. Some aminopyridines exhibited their bioactivities e.g. 2-aminopyridine was the precursor in drug processing especially in anti-histamines and piroxican (Salimon; et al. 2009: 256-264). Olegomer or polymer of 3-aminopyridine was shown to be potent anti *Staphylococcus aureus* (Akgul; & Yildirim. 2010: 1203-1208).

Objectives of the Study

1. To prepare sulfonamides (**21**) from the reaction of anthranilic acid and arenesulfonyl chlorides.

2. To synthesize mixed ligand metal complexes (**L1**-**M**-**L2**) using the sulfonamide derivatives (**21**) as the primary ligand (**L1**) and 2-, 3-, 4-aminopyridines (**L2**) as the auxiliary ligands. As well as salts of Cu(II), Zn(II), Ni(II), Mn(II) (**MY_2•nH_2O**) as metal ions.

3. To determine the structures of sulfonamides (**21**) and their metal complexes (**L1**-**M**-**L2**) using spectroscopic techniques.

Significance of the Study

1. The study provides the knowledge of sulfonamides (**21**) and related compounds.

2. The study reveals the synthesis of metal complexes from the sulfonamides and selected ligands e.g. 2-aminopyridine, 3-aminopyridine and 4-aminopyridine.

3. Bioactivities of the synthesized compounds; sulfonamides (**21**) and their metal complexes will be further evaluated.

Scope of the Study

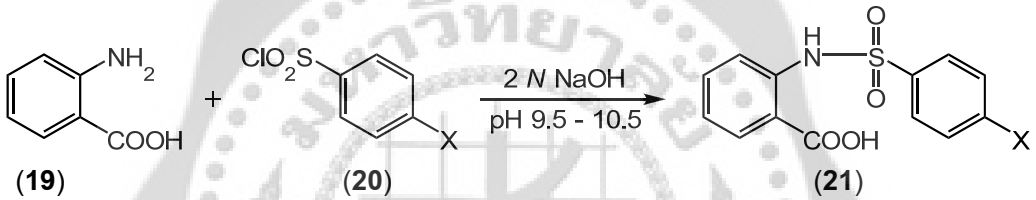
1. The arenesulfonyl chlorides used in the study are as follows:
   - 1.1 4-nitrobenzenesulfonyl chloride
   - 1.2 4-methoxybenzenesulfonyl chloride
   - 1.3 4-methylbenzenesulfonyl chloride
   - 1.4 4-chlorobenzenesulfonyl chloride
2. Ligands and metal salts used in the study are as follows:
   - 2.1 The synthesized sulfonamide derivatives (**21**)
   - 2.2 2-aminopyridine
   - 2.3 3-aminopyridine
   - 2.4 4-aminopyridine
   - 2.5 Cupric(II) chloride dihydrate
   - 2.6 Zinc(II) acetate dihydrate
   - 2.7 Nickel(II) acetate tetrahydrate
   - 2.8 Manganese(II) chloride tetrahydrate
3. Separation and purification of product were conducted using chromatographic techniques.
4. Structure determination of the compounds was performed through spectroscopic techniques; e.g. infrared spectroscopy, nuclear magnetic resonance spectroscopy, mass spectroscopy and magnetic susceptibility.

CHAPTER 2

REVIEW OF THE LITERATURE

Arenesulfonamides derivatives

Recently, significant anti-inflammatory activity of a series of *para*-substituted *N*-benzenesulfonyl derivatives of anthranilic acid was reported by Borne; et al. (Borne; et al. 1974: 615-617). The synthesis used appropriate benzenesulfonyl chlorides (**20**) reacting with anthranilic acid (**19**) to afford sulfonamide derivatives (**21**) as shown in Figure 10.



(**19**) (**20**) (**21**)

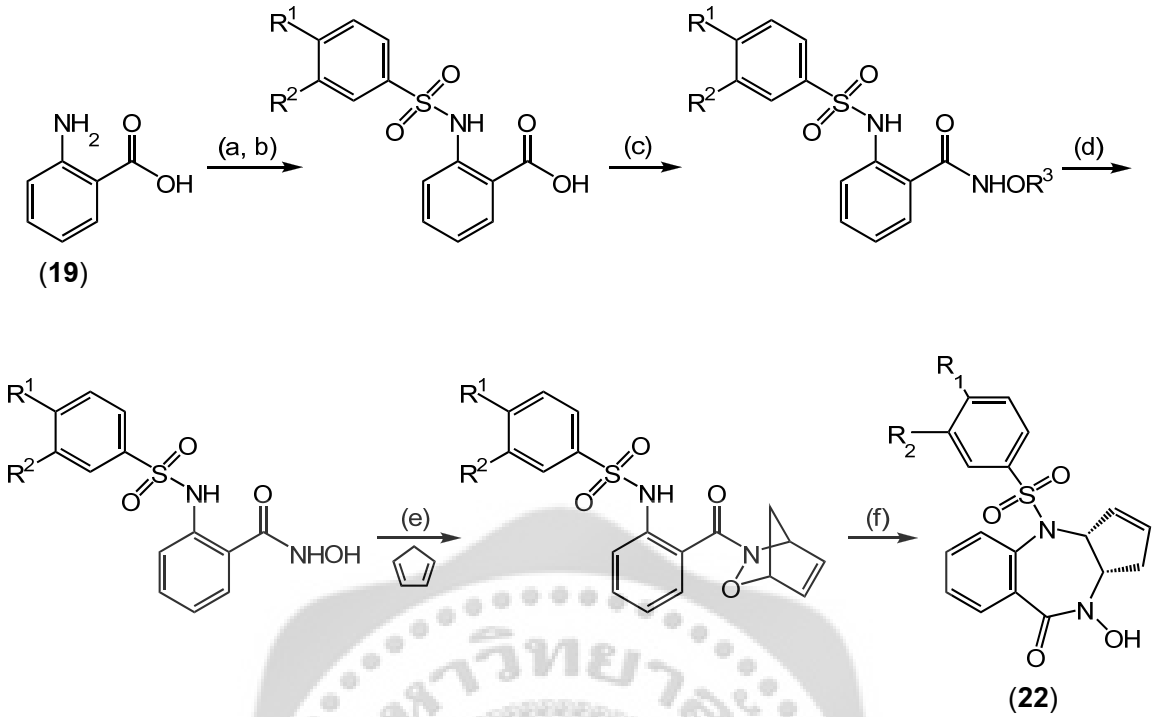
(**20a**, **21a**); X = H (**20d**, **21d**); X = F

(**20b**, **21b**); X = CH_3 (**20e**, **21e**); X = Cl

(**20c**, **21c**); X = NO_2 (**20f**, **21f**); X = Br

Figure 10 Synthesis of *para*-substituted *N*-benzenesulfonyl derivatives (**21**)

Surman; Mulvihill; & Miller (Surman; Mulvihill; & Miller. 2002: 139-141) described the synthesis of acyl-nitroso-derived hetero (**22**) by the Diels-Alder cycloaddition reaction. The synthesis involved sulfonylation of anthranilic acid with tosyl chloride to give sulfonamide derivatives which were further transformed to the compound **22** *via* multi-step reactions as outlined in Figure 11.



Method A : (a) TsCl, Na_2CO_3, H_2O; (b) HCl, 69% (two steps); (c) NH_2OBn, EDC, CH_2Cl_2, 81%; (d) H_2, Pd/C, MeOH, 99%; (e) cyclopentadiene, $NaIO_4$, MeOH, H_2O, 79%; (f) $Pd(PPh_3)_4$, THF, Δ, 20%

$\mathbf{R^1}$ = CH_3, $\mathbf{R^2}$ = H, $\mathbf{R^3}$ = Bn

Method B : (a) 3-nitrobenzenesulfonyl chloride, Na_2CO_3, H_2O, Δ;

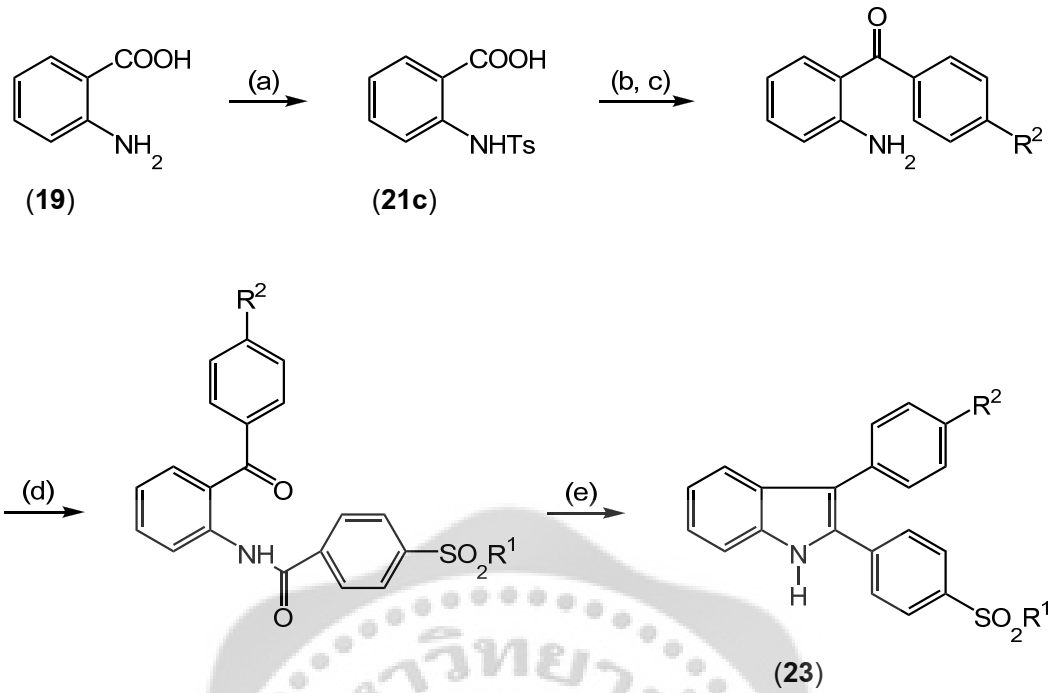
(b) HCl, 64% (two steps);

(c) NH_2OTBS, EDC, CH_2Cl_2; (d) 1 M HCl, MeOH; (e) cyclopentadiene, $NaIO_4$, MeOH, H_2O, 81% (three steps); (f) $Pd(PPh_3)_4$, THF, Δ, 38%

$\mathbf{R^1}$ = H, $\mathbf{R^2}$ = NO_2, $\mathbf{R^3}$ = TBS

Figure 11 Synthesis of acylnitroso-derived hetero (**22**)

Hu; et al. (Hu; et al. 2003: 1153-1160) studied the synthesis of 2-sulfonylphenyl-3-phenyl-indoles derivatives (**23**), which was a new inhibitor of the specific COX-2. The synthesis used sulfonamide (**21c**), as a precursor for indole ring formation, deriving from anthranilic acid (**19**) as described in Figure 12.



(a) Na_2CO_3, TsCl, 60–85 °C; (b) (i) PCl_5, 50 °C, (ii) $AlCl_3$, $C_6H_5R^2$, 80–90 °C;
(c) H_2SO_4, 120 °C; (d) 4-$R^1SO_2C_6H_4$-COCl, THF, Et_3N, rt; (e) Zn, $TiCl_4$, THF, reflux

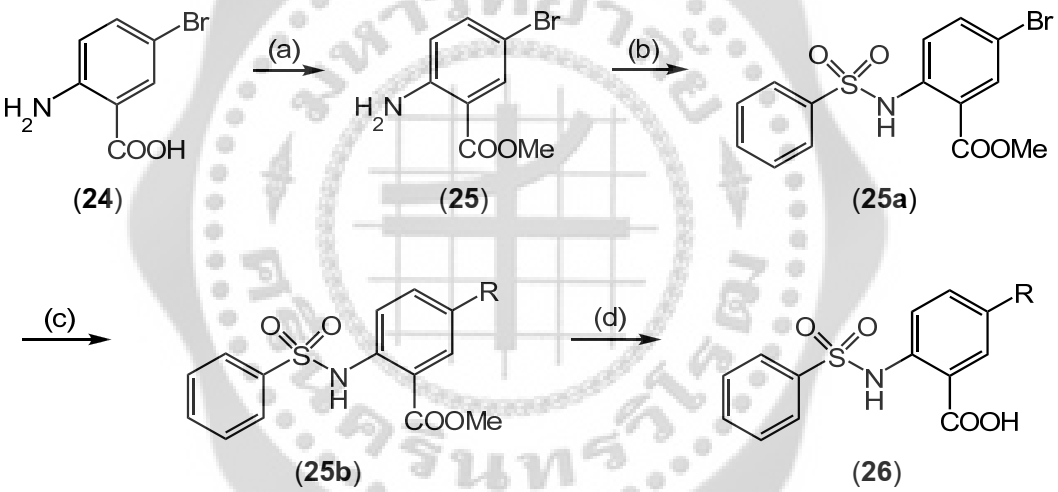
	R^1	R^2		R^1	R^2
(**23a**)	NH_2	H	(**23i**)	NH_2	4-OCH_3
(**23b**)	CH_3	H	(**23j**)	CH_3	4-OCH_3
(**23c**)	NH_2	4-F	(**23k**)	NH_2	4-CH_3
(**23d**)	CH_3	4-F	(**23l**)	CH_3	4-CH_3
(**23e**)	NH_2	4-Cl	(**23m**)	NH_2	3,4-$(CH_3)_2$
(**23f**)	CH_3	4-Cl	(**23n**)	CH_3	3,4-$(CH_3)_2$
(**23g**)	NH_2	4-Br	(**23o**)	NH_2	4-OH
(**23h**)	CH_3	4-Br	(**23p**)	NHAc	H

Figure 12 Synthesis of indole (**23**) from anthranilic acid sulfonamide

A number of sulfonamides with methionine aminopeptidase type II inhibitory effect and antiproliferative activity was studied by Kawai; et al. (Kawai; et al. 2006: 3574-3577). The sulfonamides were synthesized in various methods. For examples, 2-amino-5-bromo benzoic acid (**24**) was converted to sulfonamide derivatives of anthranilic acid (**26**) (Fig. 13). Initially, esterification of 2-amino-5-bromo benzoic acid (**24**) gave methyl ester (**25**). Further

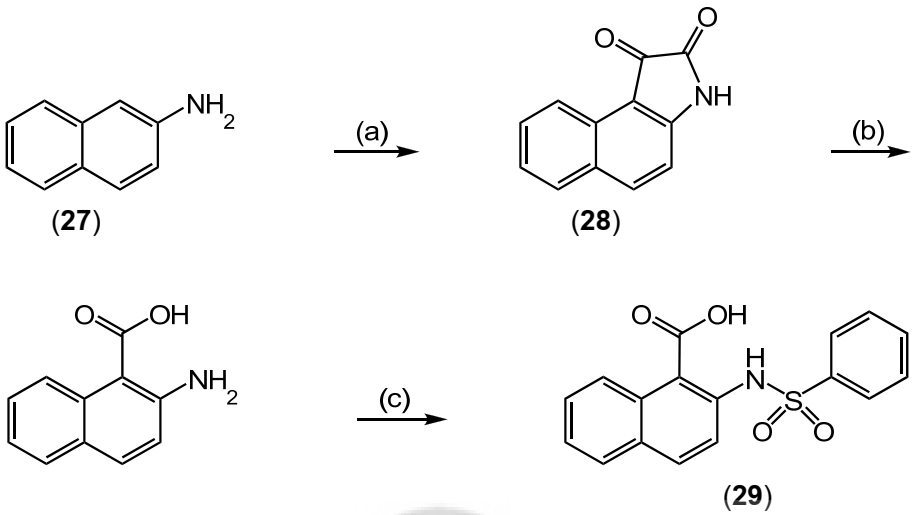
sulfonylation of methyl ester (**25**) followed by Pd-catalyzed coupling reaction afforded sulfonamide ester (**25a**). Finally, saponification of the ester (**25b**) using microwave furnished the sulfonamides (**26**). Sulfonamide derivative of naphthalene (**29**) (Fig 14) was synthesized from 2-aminonaphthalene (**27**). The amine (**27**) reacted with diethyl ketomalonate in acetic acid to form an isatin derivative (**28**) which was transformed by two steps (oxidation with alkaline hydrogen peroxide and sulfonylation) to give the final product compound **29**.

Methyl-2-hydroxynaphthalene-1-carboxylate (**30**) was hydrogenated to obtain the tetrahydro-naphthalene derivative (**31**), the synthesis was 4-step to give sulfonamide analogues, compound **32** (Fig. 15). 7-Nitro-1-tetralone (**33**) was reduced, followed by bromination to provide its hydrobromic acid salt (**34**). The reaction is more steps to afford a product, compound **35** (Fig. 16).



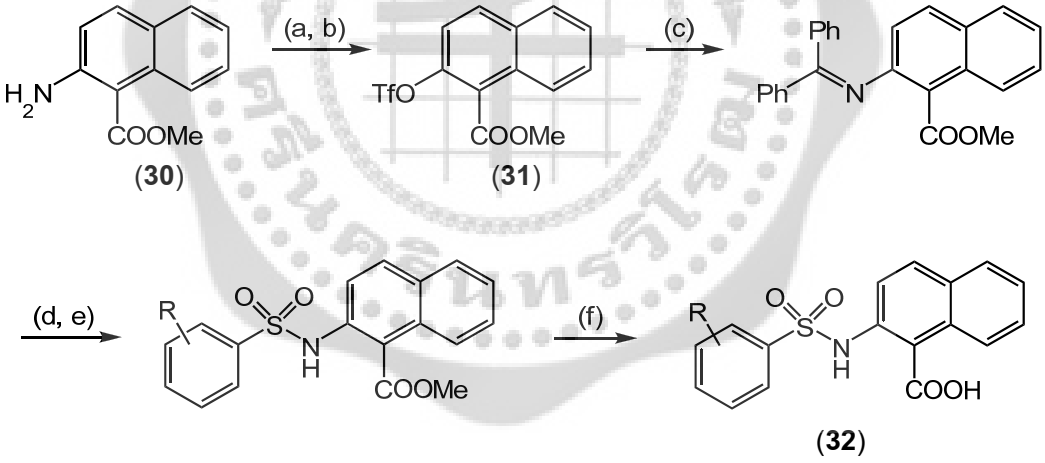
(a) HCl in MeOH; (b) $ArSO_2Cl$, Py–CH_2Cl_2; (c) RZnBr, CuI, $PdCl_2$(dppf), THF, microwave, 150 °C,10 min; (d) LiOH, dioxane–water, microwave, 160 °C

Figure 13 Synthesis of sulfonamides (**26**)



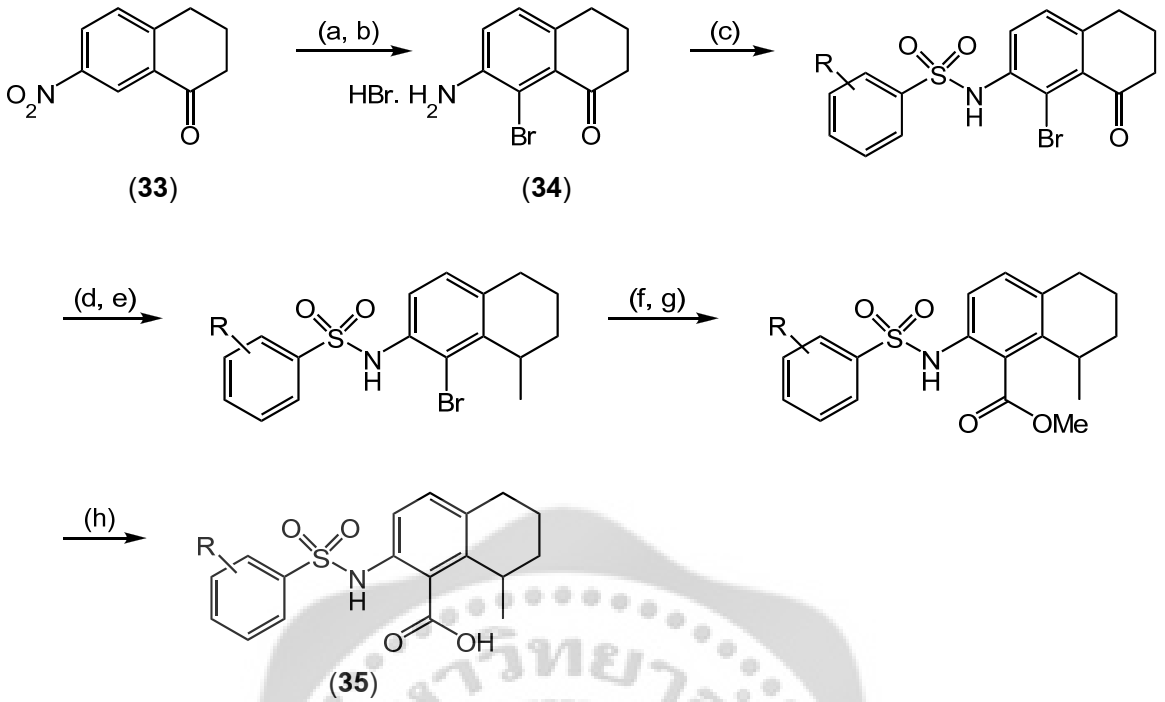
(a) diethyl ketomalonate, AcOH, 120 °C, 3 h; (b) 30% H_2O_2, 1 N NaOH;
(c) TMS–Cl, $ArSO_2Cl$, Py–CH_2Cl_2

Figure 14 Synthesis of sulfonamide (**29**)



(a) Pd/C, H_2, MeOH-H_2O; (b) Tf_2O, Py–CH_2Cl_2; (c) $Pd(OAc)_2$, xantphos, Cs_2CO_3,
$HN{=}C(Ph)_2$, dioxane; (d) HCl, THF–H_2O; (e) $ArSO_2Cl$, Py–CH_2Cl_2;
(f) microwave, LiOH, dioxane-water, 160 °C, 10 min.

Figure 15 Synthesis of sulfonamides (**32**)



(a) Fe, NH_4Cl, EtOH–H_2O (4:1); (b) Br_2, $CHCl_3$–DMF; (c) $ArSO_2Cl$, Py–CH_2Cl_2; (d) 3 M MeMgBr, THF–Et_2O; (e) *p*-TosOH toluene; (f) $PdCl_2$(dppf)-CH_2Cl_2, CO, Et_3N, MeOH; (g) Pd/C, H_2, EtOAc; (h) LiOH, dioxane–water, microwave, 160 ^{o}C, 10 min.

Figure 16 Synthesis of sulfonamides (**35**)

In general, sulfonamides were prepared from amines and sulfonyl halides in organic solvents. An evironmentally friendly method for the synthesis of sulfonamides was reported by Deng; & Mani (Deng; & Mani. 2006: 835-838). The synthesis used water as the solvent under pH control by Na_2CO_3. For example, arylsulfonyl chloride reacted with aminobenzoic (**36**) in H_2O to give sulfonamide derivatives (**37**) as shown in Figure 17.

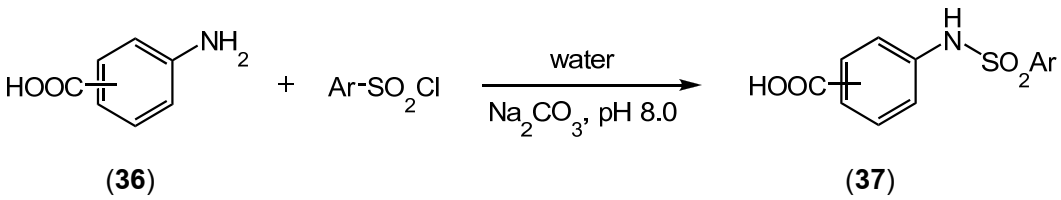
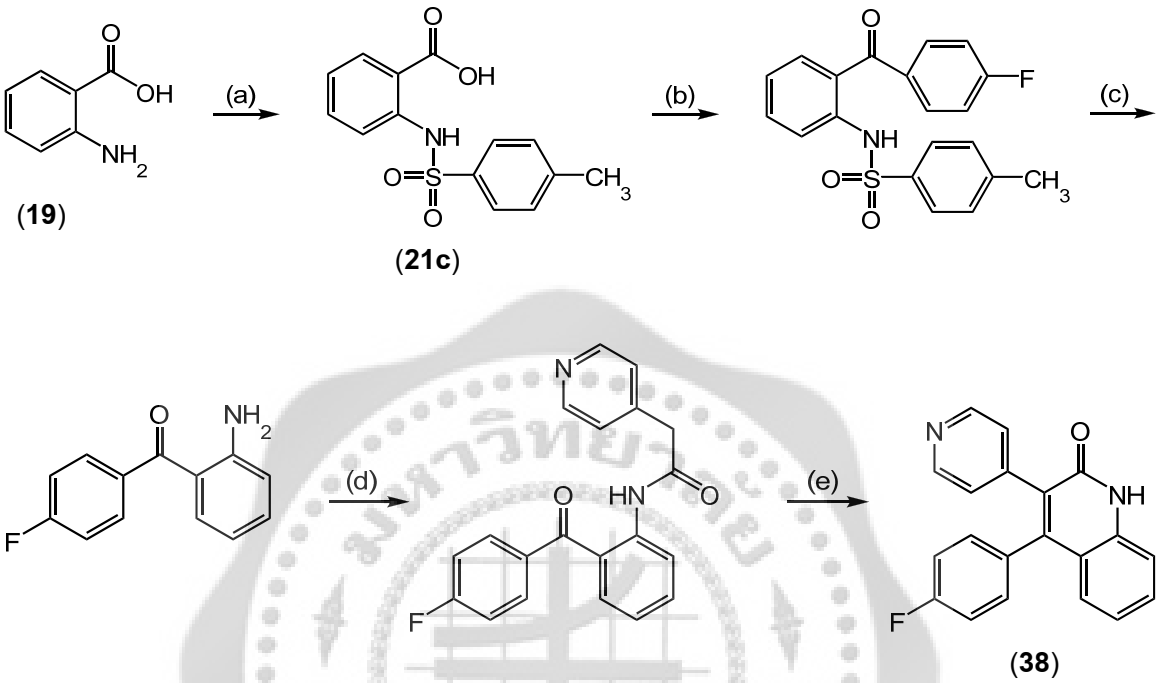


Figure 17 Synthesis of sulfonamide (**37**) from amino carboxylic acid

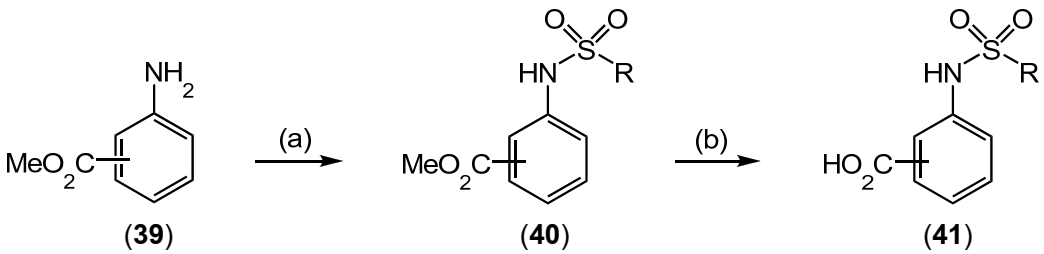
Peifer; et al. (Peifer; et al. 2007: 1213-1221) reported the synthesis of 3,4-diarylquinolone derivatives (**38**) *via* the used of anthranilic acid. The 3,4-diarylquinolones (**38**) were accomplished by multi-step reaction as depicted in Figure 18.



(a) TsCl/NaOH/H_2O, 12 h; (b) (i) fluorobenzole/PCl_5, heating for 30 min; (ii) 0 ^{o}C/$AlCl_3$ in portions, rt, 1 h; (c) HCl 0 ^{o}C; (d) DCM/pyridine, add 4-pyridylacetyl chloride in DCM, rt,12 h; (e) NH_3, rt, 2 h.

Figure 18 Synthesis of 3,4-diarylquinolone derivative (**38**)

Wydysh; et al. (Wydysh; et al. 2009: 3317-3327) investigated the synthesis of sulfonamide derivatives with glycerol 3-phosphate acyltransferase inhibitory effect. The carbomethoxy sulfonamides (**41**) were achieved through the reaction of carbomethoxy aniline (**39**) with sulfonyl chloride. Further hydrolysis of the ester sulfonamides (**40**) using potassium *t*-butoxide in diethyl ether led to required sulfonamide benzoic acids (**41**) as shown in Figure 19.



(**39**) (**40**) (**41**)

(a) RSO_2Cl, pyridine, CH_2Cl_2, 0 °C to rt.; (b) *t*-BuOK, Et_2O, H_2O, 0 °C to rt.

(**40a**);	*p*-, **R** = C_9H_{19}	(**41a**);	*p*-, **R** = C_9H_{19}
(**40b**);	*p*-, **R** = Ph	(**41b**);	*p*-, **R** = Ph
(**40c**);	*p*-, **R** = 4-ClPh	(**41c**);	*p*-, **R** = 4-ClPh
(**40d**);	*m*-, **R** = C_9H_{19}	(**41d**);	*m*-, **R** = C_9H_{19}
(**40e**);	*m*-, **R** = Ph	(**41e**);	*m*-, **R** = Ph
(**40f**);	*m*-, **R** = 4-ClPh	(**41f**);	*m*-, **R** = 4-ClPh
(**40g**);	*o*-, **R** = C_9H_{19}	(**41g**);	*o*-, **R** = C_9H_{19}
(**40h**);	*o*-, **R** = Ph	(**41h**);	*o*-, **R** = Ph
(**40i**);	*o*-, **R** = 4-ClPh	(**41i**);	*o*-, **R** = 4-ClPh

Figure 19 Synthesis of sulfonamide derivatives (**40** and **41**)

Synthesis of metal complexes of sulfonamide derivatives

It is well recognized that compounds with *O*-, *N*- and *S*-electron donors are able to form coordination compound with metal ion. For example, benzothiazole copper complexes were documented by González; et al. (González; et al. 2004: 189-198). The starting ligands were *N*-2-(5,6-dimethylbenzothiazole)toluene sulfonamide (**42a**), *N*-2-(6-chloro-benzothiazole) benzenesulfonamide (**42b**), and *N*-2-(6-chlorobenzo-thiazole) toluene-sulfonamide (**42c**) as described in Figure 20.

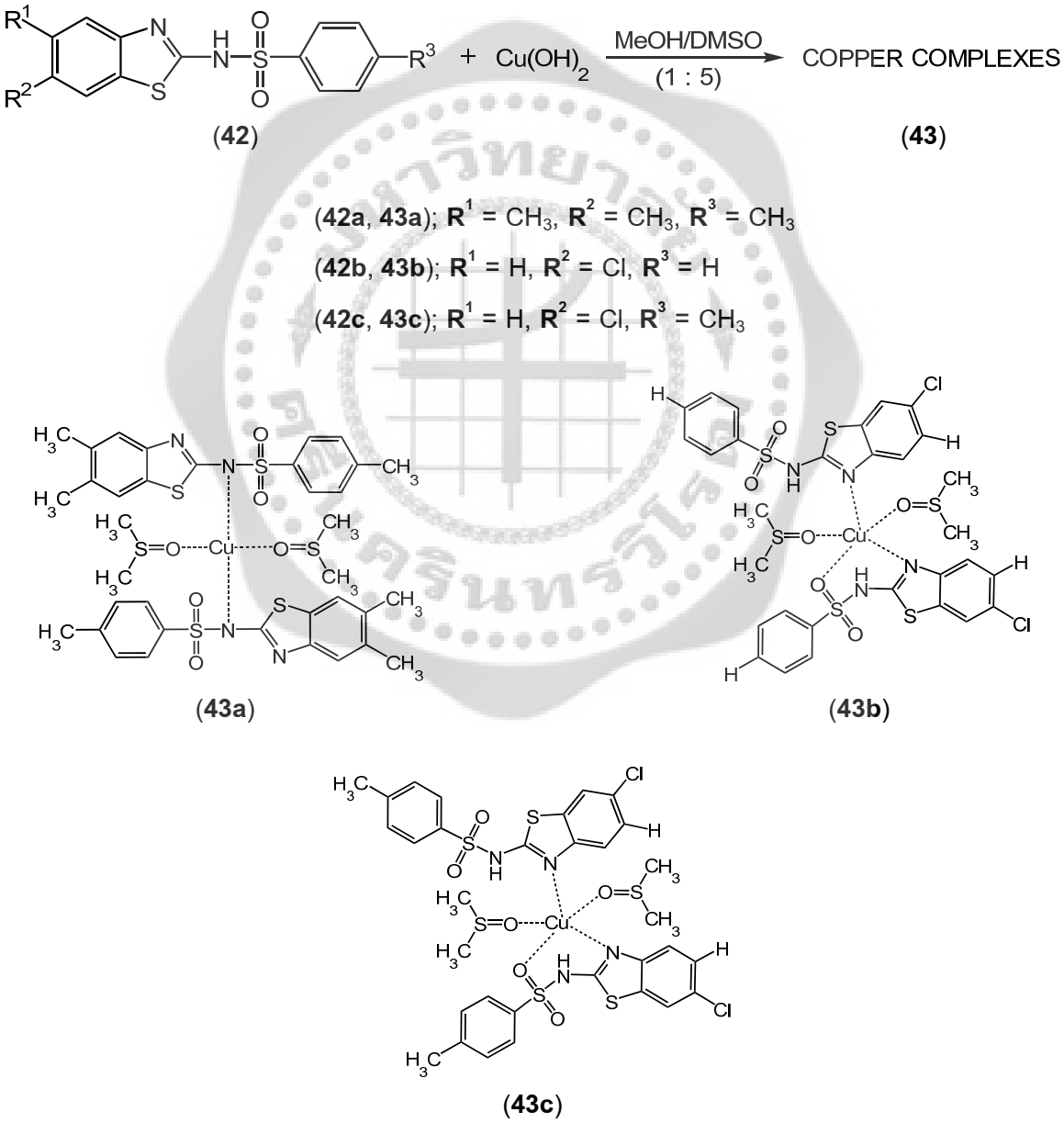


Figure 20 Synthesis of benzothiazole copper complex (**43a-c**)

Macías; et al. (Macías; et al. 2005: 1441-1448) investigated the synthesis of triazine sulfonamide copper complexes; $[Cu(bzgmes)_2(NH_3)_2]\cdot 2(C_3H_7NO)$ (**47**) and $[Cu(bzgmes)_2(DMF)_2]\cdot 2(C_3H_7NO)$ (**48**). The starting triazine sulfonamide (**46**) was prepared from the reaction of benzoguanamine (**44**) and 2-mesitylenesulfonyl chloride (**45**) as outlined in Figure 21.

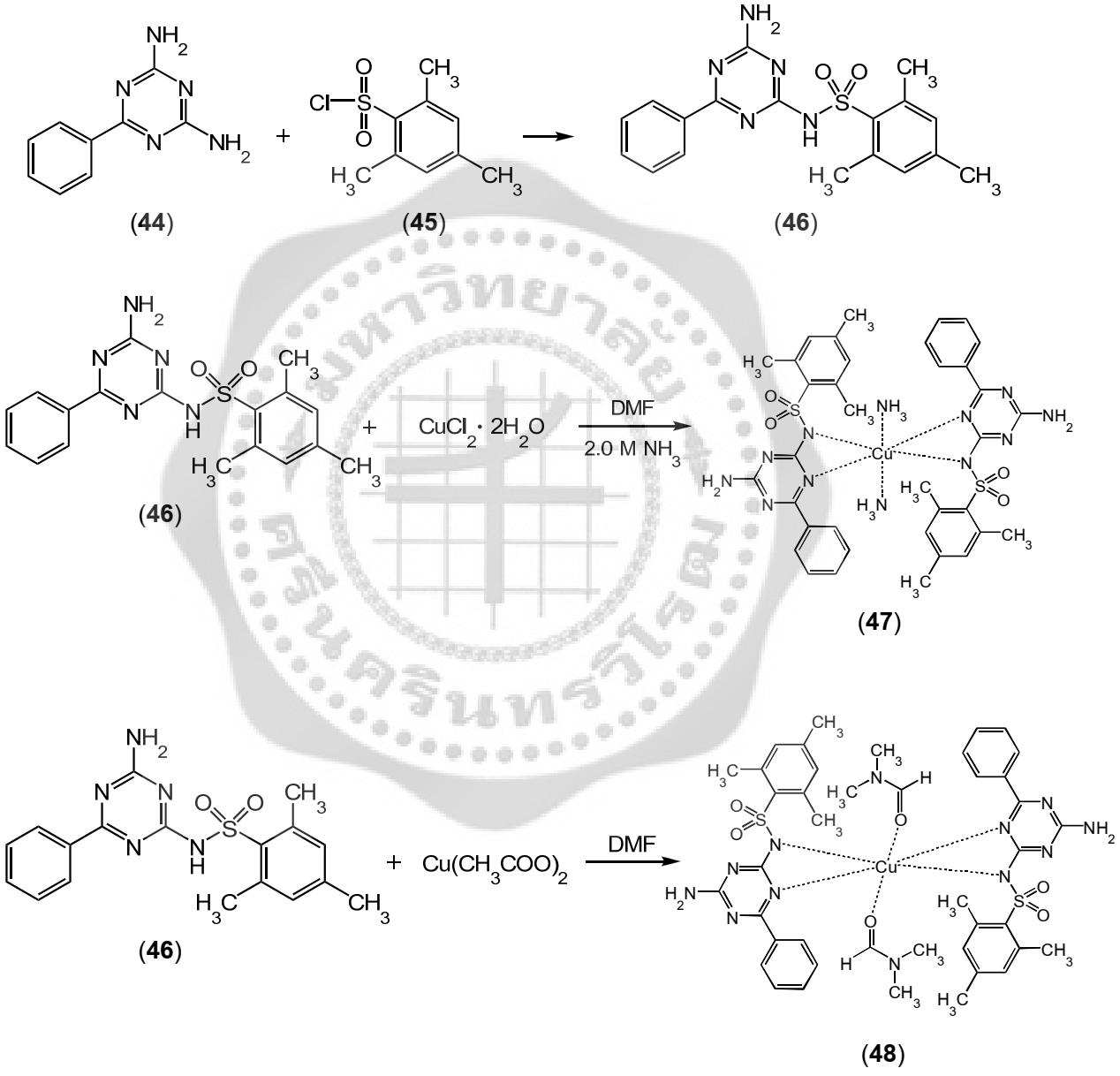


Figure 21 Synthesis of sulfonamide copper complexes (**47** and **48**)

Synthesis of thiazole sulfonamide copper complex (**52**, Fig. 22) was described by Cejudo; et al. (Cejudo; et al. 2006: 70-79). The ligand *N*-(thiazol-2-yl)benzenesulfonamides (**51**) was achieved from the reaction of 2-aminothiazole (**49**) with benzenesulfonyl chloride (**50**).

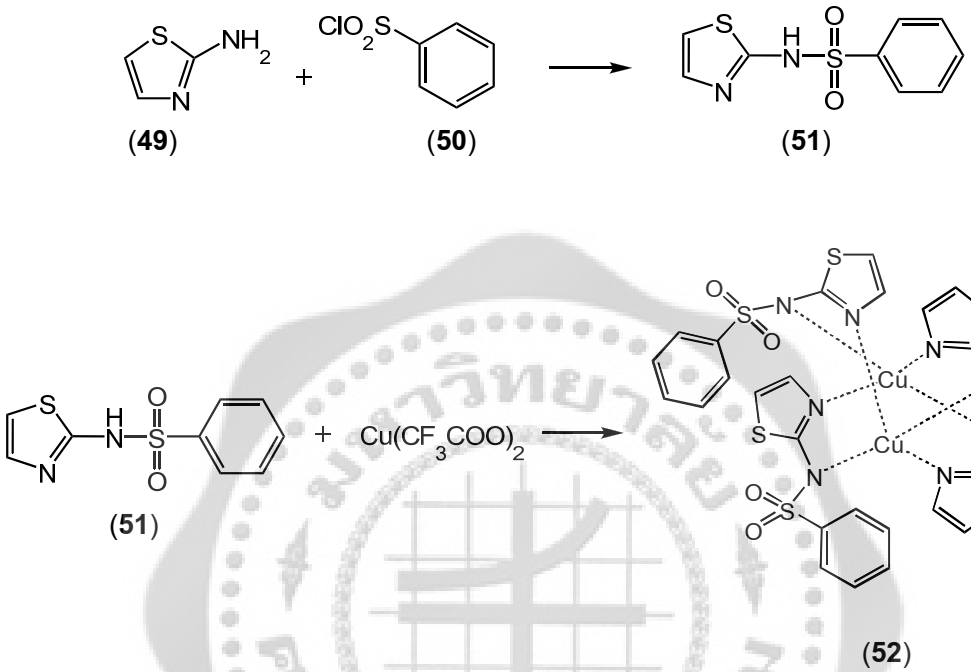


Figure 22 Synthesis of thiazole sulfonamide copper complex (**52**)

A series of antibacterial copper complexes of heterocyclic (**R**) sulfonamides were reported by Kremer; et al. (Kremer; et al. 2006: 1167-1175). Ligands sulfonamide for the synthesis were sulfadiazine (**53a**), sulfamerazine (**53b**), sulfapyridine (**53c**), sulfamethoxypyridazine (**53d**), sulfachloro-pyridazine (**53e**), sulfioxazole (**53f**), sulfamethoxazole (**53g**) and sulfamethizole (**53h**). The reaction of compound **53** with $CuSO_4 \cdot 5H_2O$ produced copper complexes of sulfonamides (**54**). An example of copper complexes such as sulfioxazole (**54f**) is illustrated in Figure 23.

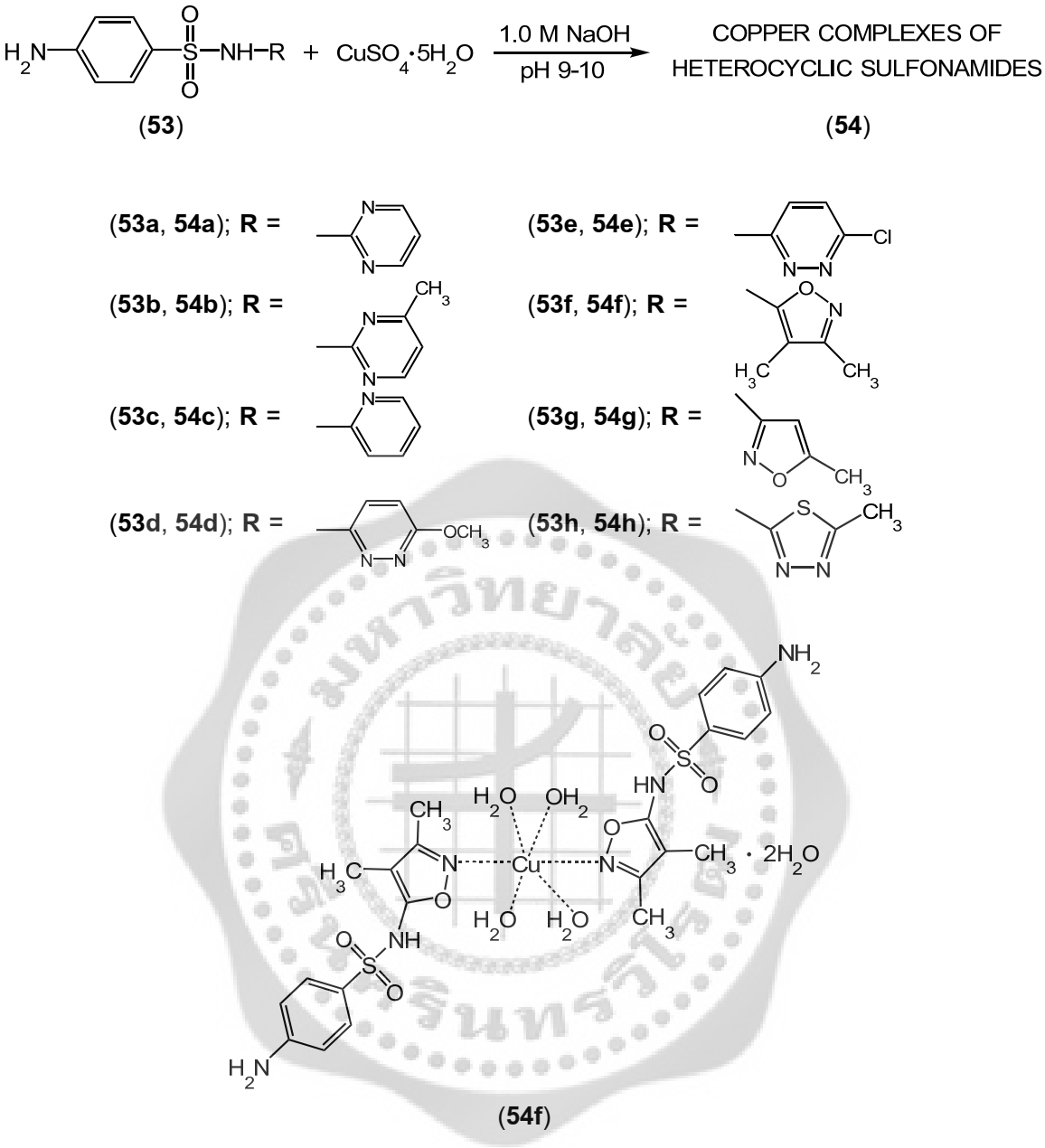


Figure 23 Synthesis of sulfonamides copper complexes (**54**)

Similarly, Mondelli; et al. (Mondelli; et al. 2008: 285-292) conducted the synthesis of sulfonamides nickel complexes (**55f** and **55c**) through the reaction of sulfioxazole (**53f**) and sulfapyridine (**53c**), with $NiSO_4 \cdot 6H_2O$. Structure of nickel complexes of sulfonamide e.g. compound **55f** is shown in Figure 24.

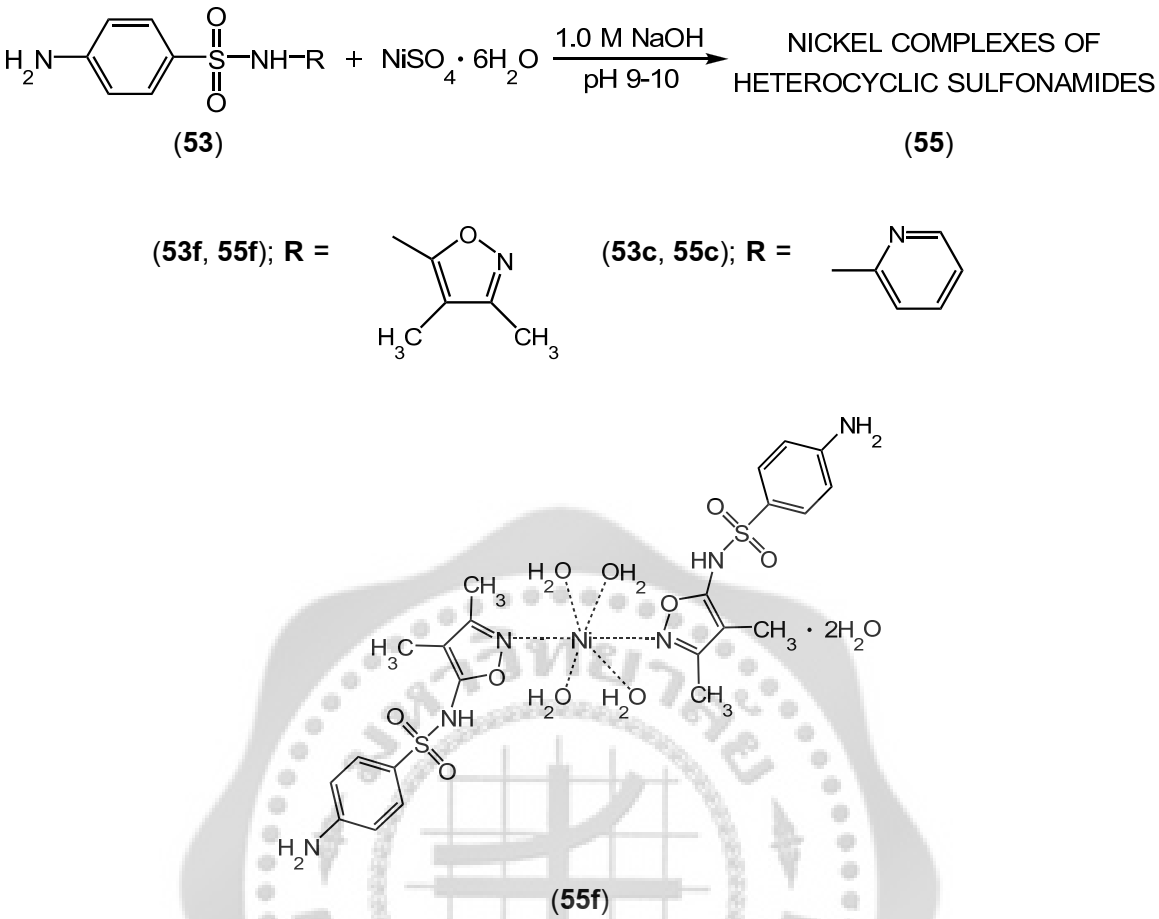
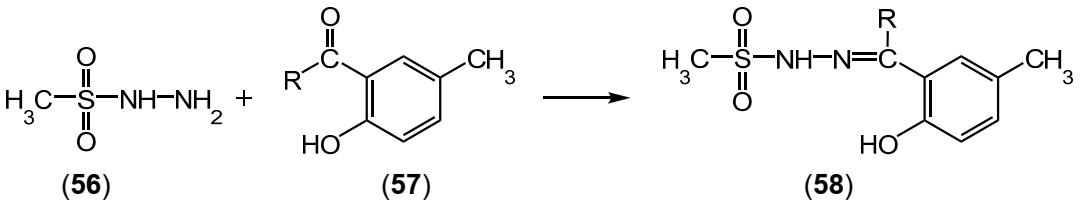


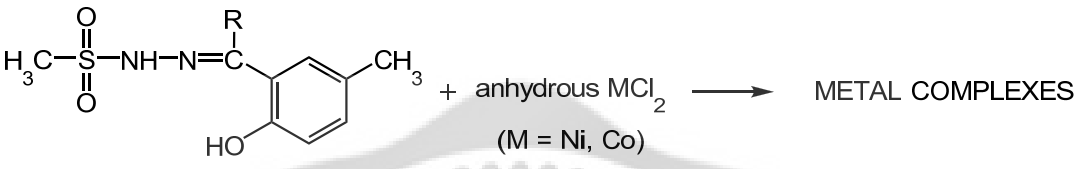
Figure 24 Synthesis of nickel complexes (**55**)

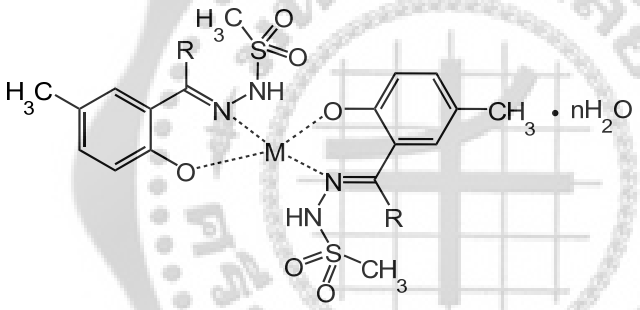
Özdemir; et al. (Özdemir; et al. 2009: 2613-2618) reported the synthesis of nickel and cobalt complexes of sulfonamide derivatives (**17**) from the reaction of hydrazone derivatives (**58**) with anhydrous $NiCl_2$ and $CoCl_2$. The hydrazone (**58**) was prepared from 5-methylsalicylaldehyde (**57a**), 5-methyl-2-hydroxy acetophenone (**57b**) with methanesulfonic acid hydrazide (**56**). Structures of metal complexes (**17**) are shown in Figure 25.



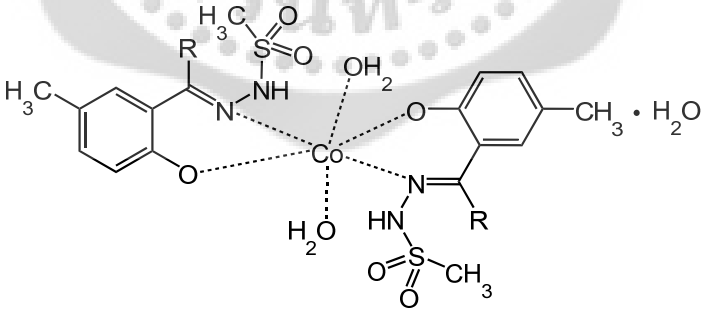
(**57a**, **58a**); R = H

(**57b**, **58b**); R = CH_3





	R	M	n
(**17a**)	H	Ni	2
(**17b**)	H	Co	2
(**17c**)	CH_3	Ni	0



(**17d**); **R** = CH_3

Figure 25 Synthesis of nickel and cobalt sulfonamide complexes (**17**)

Synthesis of aminopyridine metal complexes

Suksrichavalit; et al. (Suksrichavalit; et al. 2009: 3259-3265) reported the synthesis of copper complexes of pyridine derivatives with superoxide scavenging and antimicrobial activities. The ligands were nicotinic acid (**59**), 2-hydroxypyridine (**60**), 2-aminopyridine (**62**), 2-picolinic acid (**64**). Mixed ligand copper complexes **61**, **63** and **65** were achieved as described in Figure 26.

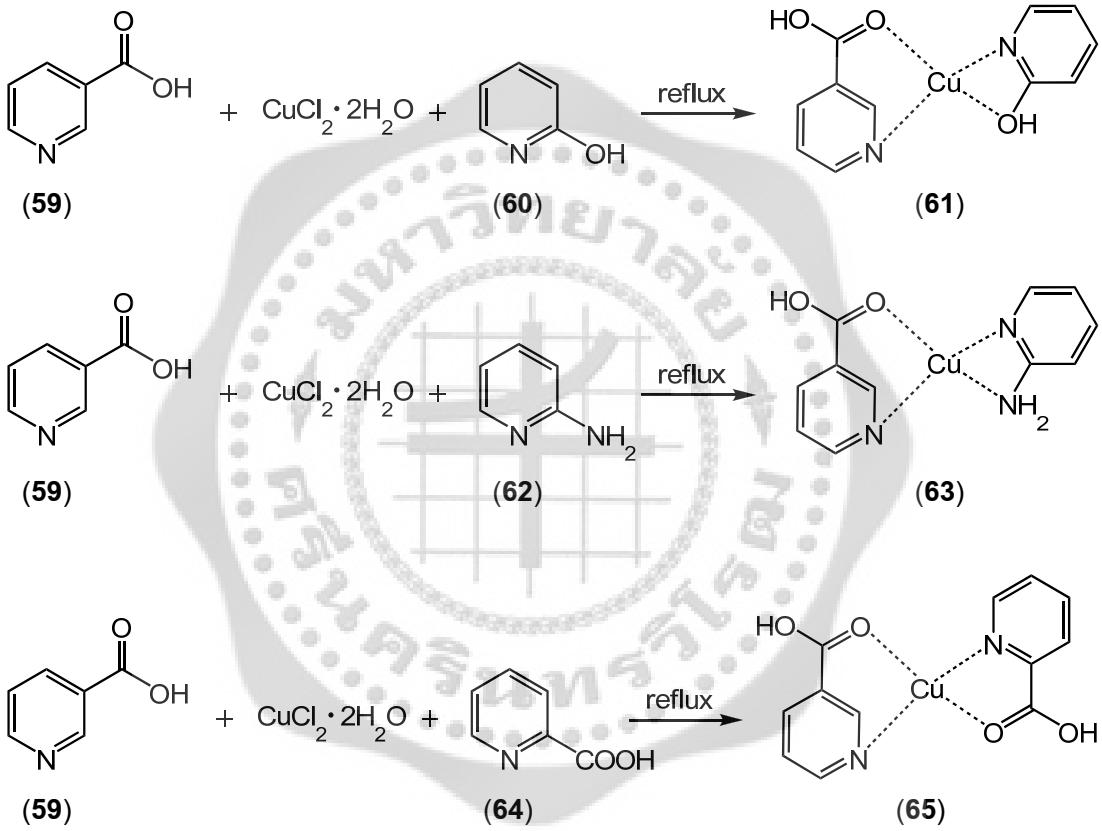
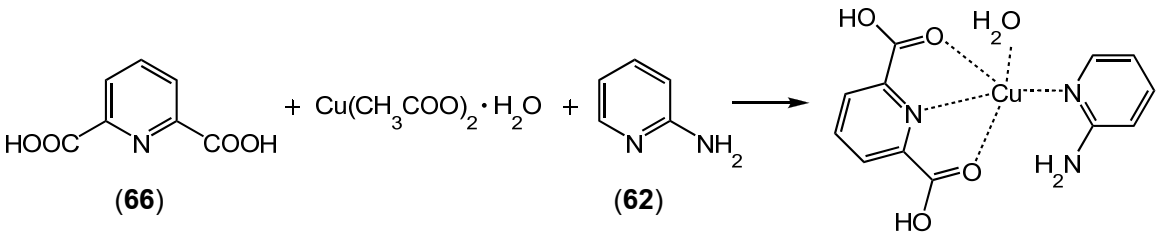


Figure 26 Synthesis of pyridines copper complexes (**61**, **63** and **65**)

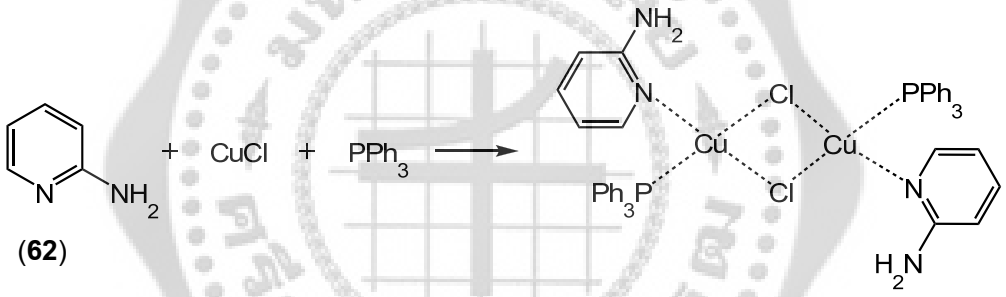
Yenikaya; et al. (Yenikaya; et al. 2009: 3526-3532) reported the synthesis of mixed ligand copper(II) complex of 2,6-pyridinedicarboxylic acid (**66**) and 2-aminopyridine (**62**) with $Cu(CH_3COO)_2{\cdot}H_2O$ as described in Figure 27.



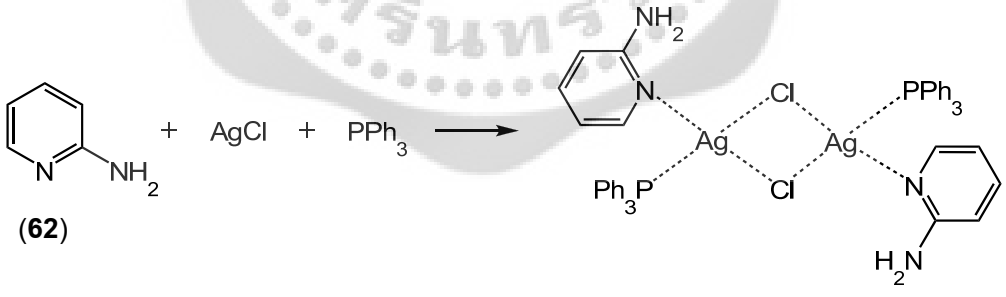
(**66**) (**62**) (**18**)

Figure 27 Synthesis of copper(II) complex (**18**)

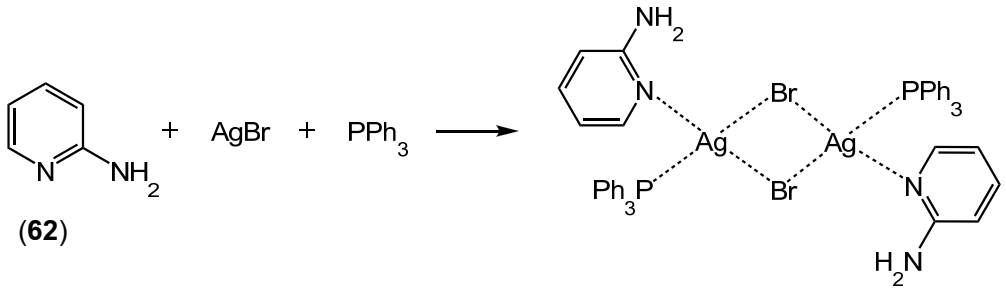
Recently, 2-aminopyridine metal complexes have been reported by Jin; et al. (Jin; et al. 2010: 441-445). 2-Aminopyridine (**62**) reacted with metal ions (CuCl, AgCl, AgBr and $AgNO_3$) and triphenyl phosphine or triphenylarsine to form mixed ligand metal complexes of copper(I) and silver(I). Their examples are **67-71** as outlined in Figure 28.



(**62**) (**67**)



(**62**) (**68**)



(**62**) (**69**)

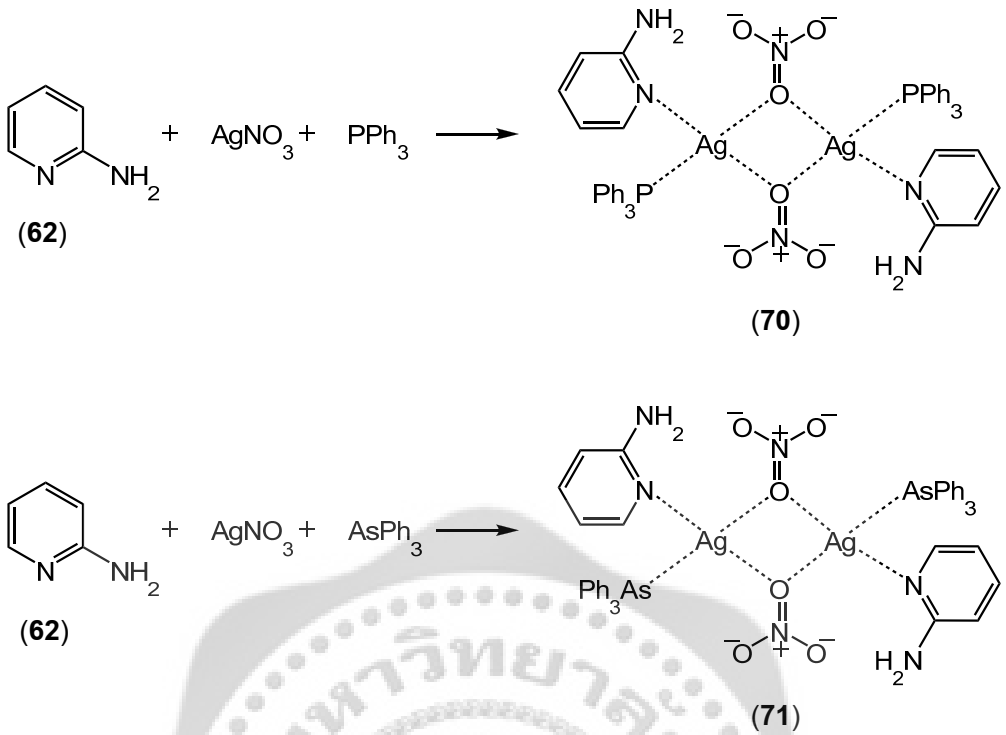


Figure 28 Synthesis of copper(I) and silver(I) complexes of 2-aminopyridine (**67-71**)

Transition metals

Transition metals have some common chemical properties. For example, they tend to form metal complexes or coordination compounds with ligands containing O-, N- and S-atoms electron donors. In general, the metal complex is a compound in which a group of atoms cluster is deposited around a single metal atom. Some metal complexes possess diverse pharmaceutical and industrial applications. However, the metals are essential in life; they play important roles in the biological systems, such as in enzymes structure and activity, transport proteins, hormonal function and specific receptor sites, if maintained at required levels. (Apostoli; 2002: 63-97).

As mentioned above, the metals are necessary in various metabolic processes e.g. Zinc (Zn) that is the most abundant intracellular components that involve in genetic stability and gene expression as well as in DNA repair and programmed cell death. In addition, deficiency in Zn has been associated with growth retardation and increasing cancer risk, but in excess it can be neurotoxic (Dreosti; 2001: 161-167). In general, Copper (Cu) is a component of various enzymes, is involved in collagen synthesis and in the normal development of connective tissues, nerves and immune system. In excess, Cu can be extremely toxic to the body or biological systems, due to its pro-oxidant activity, causing DNA damage, and it has been associated with neurodegenerative changes such as Alzheimer's disease (Llanos; & Mercer. 2002: 259–270). Manganese (Mn) is an essential trace element that plays a vital role; as an activator of several manganese metalloenzymes, including arginase, pyruvate carboxylase, glutamine synthetase, and one form of superoxide dismutase (SOD). It also is a nonspecific activator of several other enzymes. Deficiency of Mn has been induced in several animal species by feeding diets with low manganese. Signs of deficiency in animals include impaired growth, skeletal defects, depressed reproductive functions, ataxia in newborns, and defects in metabolism (Shils & Shike 2006: 326-347. and Keen; & Zidenberg-Cherr. 1996: 334-341). In addition nickel (Ni) is a trace element that has hitherto not been clearly regarded as essential, or not the element for which the human body requires an external supply. However, the beneficial effects of Ni salts for the treatment of epileptic disease and severe diarrhea, were recognized in the Middle Ages. (Kruse-Jarres. 1994: 138-141).

Bioactivities

Bioactivities of aryl- and heteroarylsulfonamide derivatives and metal complexes are summarized as shown in Tables 1-3.

TABLE 1 BIOACTIVITIES OF ARYL- AND HETEROARYLSULFONAMIDE DERIVATIVES.

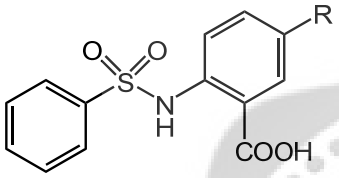
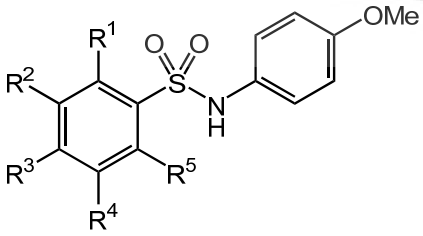
Compounds	Bioactivities	References
 (**26**) (**26a**); R = CH_3 (**26b**); R = C_2H_5 (**26c**); R = C_3H_7 (**26d**); R = C_4H_9	- Inhibition of human methionine aminopeptidase type-2 (**26a**); IC_{50} = 1 μM (**26b**); IC_{50} = 0.09 μM (**26c**); IC_{50} = 1.1 μM (**26d**); IC_{50} = 10 μM - Antiproliferation e.g. HMVEC cell line (**26a**); IC_{50} = 0.1 μM (**26b**); IC_{50} = 10 μM (**26c**); IC_{50} = 60 μM (**26d**); IC_{50} = 100 μM	- Kawai; et al. (2006: 3574-3577)
 (**11**)	- Cytotoxicity e.g. HeLa, MCF-7 and MCF-7/ADR tumor cells *in vitro* HeLa (**11a**); GI_{50} = 0.16 ± 0.07 μM (**11b**); GI_{50} = 0.22 ± 0.1 μM (**11c**); GI_{50} = 17 ± 8 μM (**11d**); GI_{50} = 21 ± 10 μM (**11e**); GI_{50} = 0.37 ± 0.2 μM	- Medina; et al. (1999: 1843-1846)

TABLE 1 (continued)

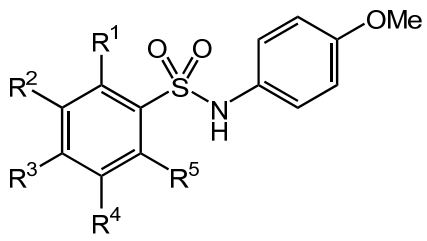
Compounds	Bioactivities	References
 (**11**)	HeLa	- Medina; et al.
	(**11f**); GI_{50} = 5.8 ± 3 μM	(1999: 1843-1846)
	(**11g**); GI_{50} = > 50 μM	
	(**11h**); GI_{50} = 3.9 ± 2.3 μM	
	(**11i**); GI_{50} = > 50 μM	
	(**11j**); GI_{50} = > 50 μM	
(**11a**); R^1 = Br, R^2 = F, R^3 = F, R^4 = F, R^5 = F	(**11k**); GI_{50} = 0.096 ± 0.05 μM	
	(**11l**); GI_{50} = 0.099 ± 0.06 μM	
(**11b**); R^1 = F, R^2 = Br, R^3 = F, R^4 = F, R^5 = F	MCF-7	
(**11c**); R^1 = F, R^2 = F, R^3 = Br, R^4 = F, R^5 = F	(**11a**); GI_{50} = 0.039 ± 0.06 μM	
	(**11b**); GI_{50} = 0.27 ± 0.3 μM	
(**11d**); R^1 = F, R^2 = F, R^3 = Cl, R^4 = F, R^5 = H	(**11c**); GI_{50} = 36 ± 7 μM	
	(**11d**); GI_{50} = 44 ± 4 μM	
(**11e**); R^1 = H, R^2 = F, R^3 = F, R^4 = F, R^5 = F	(**11e**); GI_{50} = 0.12 ± 0.1 μM	
	(**11f**); GI_{50} = 4.5 ± 4.5 μM	
(**11f**); R^1 = F, R^2 = H, R^3 = F, R^4 = F, R^5 = F	(**11g**); GI_{50} = > 50 μM	
	(**11h**); GI_{50} = 2.0 ± 0.9 μM	
(**11g**); R^1 = F, R^2 = F, R^3 = H, R^4 = F, R^5 = F	(**11i**); GI_{50} = > 50 μM	
	(**11j**); GI_{50} = > 50 μM	
(**11h**); R^1 = H, R^2 = F, R^3 = F, R^4 = F, R^5 = H	(**11k**); GI_{50} = 0.037 ± 0.04 μM	
	(**11l**); GI_{50} = 0.029 ± 0.04 μM	
(**11i**); R^1 = H, R^2 = H, R^3 = F, R^4 = F, R^5 = F		
(**11j**); R^1 = F, R^2 = H, R^3 = F, R^4 = H, R^5 = F	MCF-7/ADR	
	(**11a**); GI_{50} = 0.16 ± 0.08 μM	
(**11k**); R^1 = F, R^2 = Cl, R^3 = F, R^4 = Cl, R^5 = F	(**11b**); GI_{50} = 0.19 ± 0.09 μM	
	(**11c**); GI_{50} = 21 ± 9 μM	
(**11l**); R^1 = F, R^2 = F, R^3 = F, R^4 = F, R^5 = F	(**11d**); GI_{50} = 22 ± 9 μM	
	(**11e**); GI_{50} = 0.40 ± 0.3 μM	

TABLE 1 (continued)

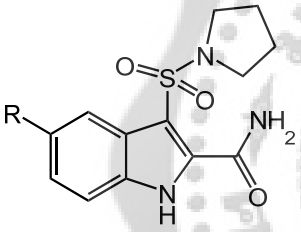
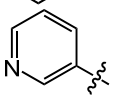
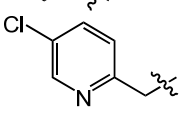
Compounds	Bioactivities	References
	MCF-7/ADR (**11f**); GI_{50} = 4.5 ± 4.5 μM (**11g**); GI_{50} = > 50 μM (**11h**); GI_{50} = 3.4 ± 1 μM (**11i**); GI_{50} = > 50 μM (**11j**); GI_{50} = > 50 μM (**11k**); GI_{50} = 0.058 ± 0.03 μM (**11l**); GI_{50} = 0.058 ± 0.05 μM	- Medina; et al. (1999: 1843-1846)
 (**12**) (**12a**); R = Cl (**12b**); R = CN (**12c**); R =  (**12d**); R =  (**12e**); R =  (**12f**); R =  (**12g**); R = 	Anti-HIV activity WT RT (**12a**); IC_{50} = 3.9 nM (**12b**); IC_{50} = 9.1 nM (**12c**); IC_{50} = 940 nM (**12d**); IC_{50} = 430 nM (**12e**); IC_{50} = 550 nM (**12f**); IC_{50} = 2200 nM (**12g**); IC_{50} = 59 nM SPREAD (**12a**); CIC_{50} = < 7.8 nM (**12b**); CIC_{50} = 16 nM (**12c**); CIC_{50} = 160 nM (**12d**); CIC_{50} = 630 nM (**12e**); CIC_{50} = 1300 nM (**12f**); CIC_{50} = 310 nM (**12g**); CIC_{50} = nd	- Zhao; et al. (2008: 554-559)

TABLE 1 (continued)

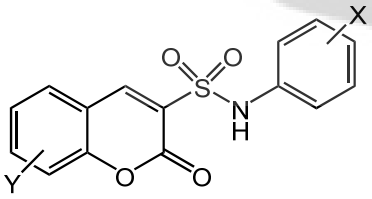
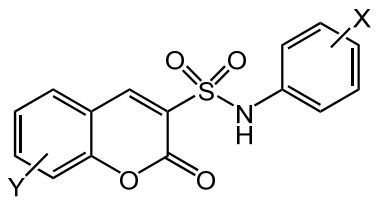
Compounds	Bioactivities	References
	K103N RT (**12a**); IC_{50} = 1963 nM (**12b**); IC_{50} = 2300 nM (**12c**); IC_{50} = nd (**12d**); IC_{50} = nd (**12e**); IC_{50} = nd (**12f**); IC_{50} = nd (**12g**); IC_{50} = 8200 nM Y181C RT (**12a**); IC_{50} = 48 nM (**12b**); IC_{50} = > 10000 nM (**12c**); IC_{50} = nd (**12d**); IC_{50} = nd (**12e**); IC_{50} = nd (**12f**); IC_{50} = nd (**12g**); IC_{50} = > 10000 nM	- Zhao; et al. (2008: 554-559)
 (**13**)	Growth inhibition of cultured tumor cells. BT20 (**13a**); GI_{50} = 16 μM (**13b**); GI_{50} = 27 μM (**13c**); GI_{50} = 52 μM (**13d**); GI_{50} = 65 μM (**13e**); GI_{50} = 54 μM (**13f**); GI_{50} = 68 μM (**13g**); GI_{50} = 18 μM (**13h**); GI_{50} = 64 μM	- Reddy; et al. (2004: 4093-4097)

TABLE 1 (continued)

Compounds	Bioactivities	References
 (**13**)	BT20 (**13i**); GI_{50} = 17 μM (**13j**); GI_{50} = 12 μM DU145 (**13a**); GI_{50} = 15 μM (**13b**); GI_{50} = 22 μM (**13c**); GI_{50} = 57 μM (**13d**); GI_{50} = 42 μM (**13e**); GI_{50} = 48 μM (**13f**); GI_{50} = 56 μM (**13g**); GI_{50} = 25 μM (**13i**); GI_{50} = 52 μM (**13j**); GI_{50} = 14 μM (**13h**); GI_{50} = 12 μM H157 (**13a**); GI_{50} = 18 μM (**13b**); GI_{50} = 28 μM (**13c**); GI_{50} = 74 μM (**13d**); GI_{50} = 76 μM (**13e**); GI_{50} = 72 μM (**13f**); GI_{50} = 78 μM (**13g**); GI_{50} = 32 μM (**13i**); GI_{50} = 74 μM (**13j**); GI_{50} = 16 μM (**13h**); GI_{50} = 15 μM	- Reddy; et al. (2004: 4093-4097)

	X	**Y**
(**13a**);	4-OMe	8-Br
(**13b**);	4-OMe	6-Cl
(**13c**);	4-OMe	8-OEt
(**13d**);	4-OMe, 3-OH	6-Cl
(**13e**);	4-F, 3-NH_2	8-OEt
(**13f**);	4-F, 3-NH_2	6-OMe
(**13g**);	4-Br	6-OMe
(**13h**);	4-Br	8-OEt
(**13i**);	4-Br	8-Cl
(**13j**);	4-Br	8-Br

TABLE 1 (continued)

Compounds	Bioactivities	References
	DLD-1	- Reddy; et al. (2004:
	(**13a**); GI_{50} = 20 μM	4093-4097)
	(**13b**); GI_{50} = 32 μM	
	(**13c**); GI_{50} = 78 μM	
	(**13d**); GI_{50} = 82 μM	
	(**13e**); GI_{50} = 80 μM	
	(**13f**); GI_{50} = 92 μM	
	(**13g**); GI_{50} = 38 μM	
	(**13i**); GI_{50} = 85 μM	
	(**13j**); GI_{50} = 18 μM	
	(**13h**); GI_{50} = 14 μM	
	K562	
	(**13a**); GI_{50} = 14 μM	
	(**13b**); GI_{50} = 23 μM	
	(**13c**); GI_{50} = 48 μM	
	(**13d**); GI_{50} = 51 μM	
	(**13e**); GI_{50} = 42 μM	
	(**13f**); GI_{50} = 44 μM	
	(**13g**); GI_{50} = 27 μM	
	(**13i**); GI_{50} = 58 μM	
	(**13j**); GI_{50} = 11 μM	
	(**13h**); GI_{50} = 16 μM	

TABLE 1 (continued)

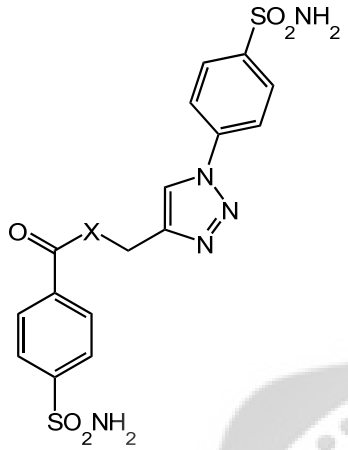
Compounds	Bioactivities	References
 (**14**) (**14a**); **X** = O (**14b**); **X** = NH	Antimycobacterials; *M. smegmatis* (**14a**); MIC_{50} = < 25 µg/mL (**14b**); MIC_{50} = ~100 µg/mL *C. albicans* (**14a**); MIC_{50} = ~100 µg/mL (**14b**); MIC_{50} = NA Bacterial strains (*E. coli*, *S. aureus*, *V. Harveyi*) (**14a**); MIC_{50} = NA (**14b**); MIC_{50} = NA (NA = not active)	- Wilkinson ; et al. (2007: 1355-1357)

TABLE 2 BIOACTIVITIES OF ARYL- AND HETEROARYLSULFONAMIDE METAL COMPLEXES.

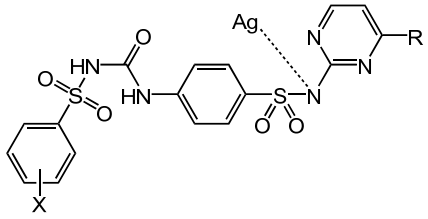
Compounds	Bioactivities	References
 (**15**) (**15a**); X = H, R = H (**15b**); X = 4-F, R = H (**15c**); X = 4-Cl, R = H (**15d**); X = 4-Me, R = H (**15e**); X = 2-Me, R = H (**15f**); X = H, R = Me (**15g**); X = 4-F, R = Me (**15h**); X = 4-Cl, R = Me (**15i**); X = 4-Me, R = Me (**15j**); X = 2-Me, R = Me	- Antimicrobial activity *A. flavus* C1150 (**15a**); MIC = 9 μg/mL (**15b**); MIC = 4 μg/mL (**15c**); MIC = 5 μg/mL (**15d**); MIC = 4 μg/mL (**15e**); MIC = 6 μg/mL (**15f**); MIC = 11 μg/mL (**15g**); MIC = 3 μg/mL (**15h**); MIC = 6 μg/mL (**15i**); MIC = 6 μg/mL (**15j**); MIC = 6 μg/Ml *A. niger* C418 (**15a**); MIC = 12 μg/mL (**15b**); MIC = 4 μg/mL (**15c**); MIC = 8 μg/mL (**15d**); MIC = 6 μg/mL (**15e**); MIC = 9 μg/mL (**15f**); MIC = 13 μg/mL (**15g**); MIC = 3.5 μg/mL (**15h**); MIC = 5 μg/mL (**15i**); MIC = 8 μg/mL (**15j**); MIC = 9 μg/mL *C. albicans* C316 (**15a**); MIC = 2.5 μg/mL (**15b**); MIC = 1.8 μg/mL (**15c**); MIC = 1.9 μg/mL (**15d**); MIC = 2.7 μg/mL	- Mastrolorenzo; Scozzafava; & Supuran. (2000: 99-107)

TABLE 2 (continued)

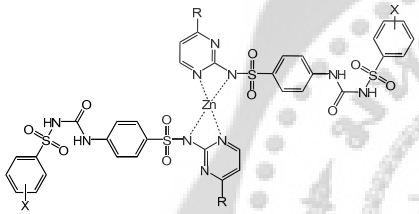
Compounds	Bioactivities	References
	C. albicans C316 (**15e**); MIC = 2.5 µg/mL (**15f**); MIC = 2.1 µg/mL (**15g**); MIC = 1.2 µg/mL (**15h**); MIC = 1.9 µg/mL (**15i**); MIC = 2.7 µg/mL (**15j**); MIC = 2.9 µg/mL	- Mastrolorenzo; Scozzafava; & Supuran. (2000: 99-107)
 (**16**) (**16a**); X = H, R = H (**16b**); X = 4-F, R = H (**16c**); X = 4-Cl, R = H (**16d**); X = 4-Me, R = H (**16e**); X = 2-Me, R = H (**16f**); X = H, R = Me (**16g**); X = 4-F, R = Me (**16h**); X = 4-Cl, R = Me (**16i**); X = 4-Me, R = Me (**16j**); X = 2-Me, R = Me	- Antimicrobial activity *A. flavus* C1150 (**16a**); MIC = 15 µg/mL (**16b**); MIC = 12 µg/mL (**16c**); MIC = 8 µg/mL (**16d**); MIC = 10 µg/mL (**16e**); MIC = 12 µg/mL (**16f**); MIC = 12 µg/mL (**16g**); MIC = 10 µg/mL (**16h**); MIC = 9 µg/mL (**16i**); MIC = 10 µg/mL (**16j**); MIC = 12 µg/mL *A. niger* C418 (**16a**); MIC = 12 µg/mL (**16b**); MIC = 10 µg/mL (**16c**); MIC = 10 µg/mL (**16d**); MIC = 11 µg/mL (**16e**); MIC = 19 µg/mL (**16f**); MIC = 9 µg/mL (**16g**); MIC = 12 µg/mL (**16h**); MIC = 10 µg/mL	- Mastrolorenzo; Scozzafava; & Supuran. (2000: 99-107)

TABLE 2 (continued)

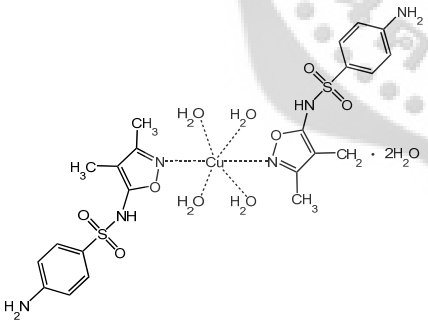
Compounds	Bioactivities	References
	A. niger C418 (**16i**); MIC = 13 µg/mL (**16j**); MIC = 12 µg/mL *C. albicans* C316 (**16a**); MIC = 8 µg/mL (**16b**); MIC = 7 µg/mL (**16c**); MIC = 2 µg/mL (**16d**); MIC = 9 µg/mL (**16e**); MIC = 10 µg/mL (**16f**); MIC = 6 µg/mL (**16g**); MIC = 5 µg/mL (**16h**); MIC = 2.1 µg/mL (**16i**); MIC = 6 µg/mL (**16j**); MIC = 8 µg/mL	- Mastrolorenzo; Scozzafava; & Supuran. (2000: 99-107)
 (**54f**)	- Antimicrobial activity *S. aureus* ATCC 29213 MIC = 128 µg/mL *E. coli* ATCC 25922 MIC = 128 µg/mL	- Kremer; et al. (2006: 1167-1175)

TABLE 2 (continued)

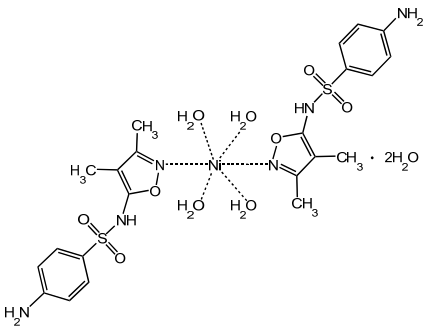
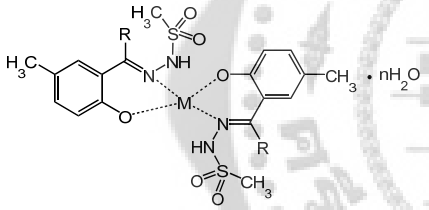
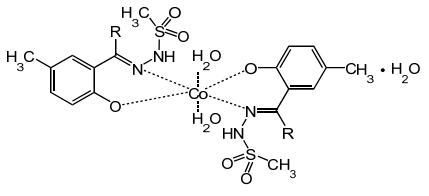
Compounds	Bioactivities	References
 (**55f**)	- Antimicrobial activity *S. aureus* MIC = 8 μg/mL *E. coli* MIC = 64 μg/mL *M. tuberculosis* MIC = 250 μg/mL	- Mondelli; et al. (2008: 285-292)
 (**17**) (**17a**); R = H, M = Ni, n = 2 (**17b**); R = H, M = Co, n = 2 (**17c**); R = CH_3, M = Ni, n = 1  (**17d**); R = CH_3	- Antimicrobial activity *B. subtilis* RSKK 244 (**17a**); MIC = 430 μg/mL (**17b**); MIC = 604 μg/mL (**17c**); MIC = 433 μg/mL (**17d**); MIC = 410 μg/mL *B. magatrium* RSKK 5117 (**17a**); MIC = 513 μg/mL (**17b**); MIC = 549 μg/mL (**17c**); MIC = 541 μg/mL (**17d**); MIC = 550 μg/mL *S. aureus* ATCC 25923 (**17a**); MIC = 280 μg/mL (**17b**); MIC = 410 μg/mL (**17c**); MIC = 384 μg/mL (**17d**); MIC = 413 μg/mL *S. enderitidis* ATCC 13076 (**17a**); MIC = 430 μg/mL (**17b**); MIC = 549 μg/mL (**17c**); MIC = 433 μg/mL (**17d**); MIC = 550 μg/mL	- Özdemir; et al. (2009: 2613-2618)

TABLE 2 (continued)

Compounds	Bioactivities	References
	E. coli ATCC 11230	- Özdemir; et al.
	(**17a**); MIC = 540 µg/mL	(2009: 2613-2618)
	(**17b**); MIC = 604 µg/mL	
	(**17c**); MIC = 541 µg/mL	
	(**17d**); MIC = 610 µg/mL	

TABLE 3 BIOACTIVITIES OF AMINOPYRIDINES METAL COMPLEXES.

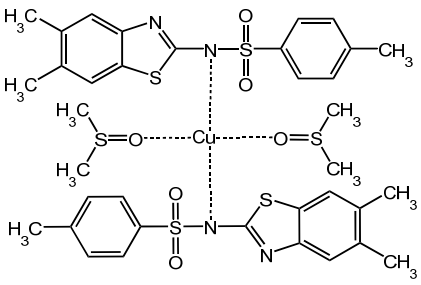
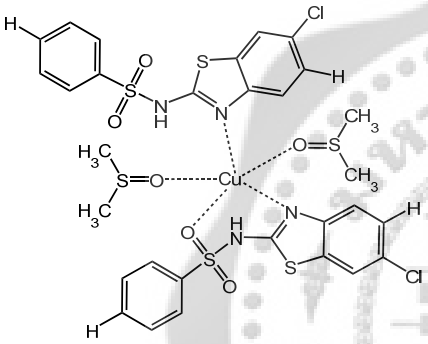
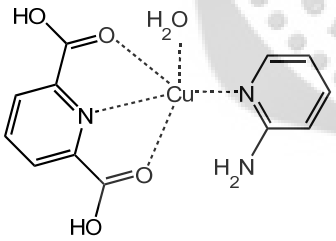
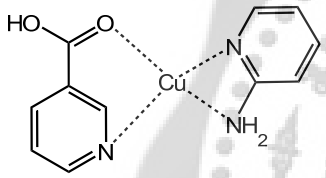
Compounds	Bioactivities	References
 (**43a**)	- Superoxide dismutase (SOD) activity (**43a**); IC_{50} = 0.193 μM (**43b**); IC_{50} = 0.188 μM	- González; et al. (2004: 189-198)
 (**43b**)		
 (**18**)	- Antimicrobial activity *E. coli* NRRL B-3008 MIC = 0.5 mg/mL *P. aeruginosa* ATCC 27853 MIC = 0.5 mg/mL *P. vulgaris* NRRL B-123 MIC = 0.25 mg/mL *S. aureus* ATCC 6538 MIC = 0.5 mg/mL *C. albicans* Clinical isolate MIC = 0.125 mg/mL *C. albicans* ATCC 90028 MIC = 0.0625 mg/mL *C. albicans* NRRL Y-12983 MIC = 0.125 mg/mL	- Yenikaya; et al. (2009: 3526-3532)

TABLE 3 (continued)

Compounds	Bioactivities	References
	C. glabrata Clinical Isolate MIC = 0.125 mg/mL *C. krusei* NRRL Y-7179 MIC = 0.125 mg/mL *C. parapsilos*is NRRL Y-12696 MIC = 0.125 mg/mL *C. tropicalis* NRRL Y-12968 MIC = 0.125 mg/mL	- Yenikaya; et al. (2009: 3526-3532)
 (**63**)	- Superoxide dismutase (SOD) activity IC_{50} = 50.32 μM	- Suksrichavalit; et al. (2009: 3259-3265)

CHAPTER 3

EXPERIMENTAL

1. General Techniques

Solvents and Chemicals

1. Anthranilic acid (Analytical grade; Carlo erba)
2. 4-Nitrobenzenesulfonyl chloride (Analytical grade; Fluka)
3 4-Methoxybenzenesulfonyl chloride (Analytical grade; Acros organic)
4. 4-Methylbenzenesulfonyl chloride (Analytical grade; Acros organic)
5. 4-Chlorobenzenesulfonyl chloride (Analytical grade; Acros organic)
6. 2-Aminopyridine (Analytical grade; Acros organic)
7. 3-Aminopyridine (Analytical grade; Acros organic)
8. 4-Aminopyridine (Analytical grade; Acros organic)
9. Cupric(II) chloride dihydrate (Analytical grade; J.T. baker)
10. Zinc(II) acetate dihydrate (Analytical grade; Carlo erba)
11. Nickel(II) acetate tetrahydrate (Analytical grade; Fluka)
12. Manganese(II) chloride tetrahydrate (Analytical grade; Carlo erba)
13. Sodium carbonate (Analytical grade; Qrec chemical)
14. Hydrochloric acid (Analytical grade; J.T. baker)
15. Anhydrous sodium sulphate (Analytical grade; Ajax chemical)
16. Hexane (Commercial grade)
17. Dichloromethane (Commercial grade)
18. Acetone (Commercial grade)
19. Ethyl acetate (Commercial grade)
20. Ethanol (Commercial grade)
21. Methanol (Commercial grade)
22. Absolute methanol (Analytical grade; BDH chemicals)
23. Silica gel for column chromatography

    Silica gel (< 0.063 mm, Merck)
24. Pre-coated TLC aluminium sheets of silica gel 60 GF 254 (Merck)

Instruments

1. Glass wares
2. Glass chromatography columns
3. UV lamp (Spectroline Model ENF240C/EF and CM-10)
4. Melting point apparatus (Griffin)
5. 4-Decimal balance (Mettler AE200)
6. Rotary evaporator (Buchi Rotavapor R-114)
7. Fourier Transform infrared spectrophotometer
   (Perkin Elmer FT-IR spectrum Bx)
8. Nuclear magnetic resonance spectrometer (Bruker Avance 300)

2. General Procedure

2.1 Synthesis of Sulfonamides

A solid mixture of anthranilic acid (1.0 eqiv.mol) and substituted arenesulfonyl chloride (3.0 eqiv.mol), was suspended in 20 mL of water. Saturated Na_2CO_3 was added to basify the suspension, then further stirred at room temperature. The reaction was mornitored by TLC (Thin Layer Chromatography). When the reaction was completed, conc.HCl was added to the suspension, precipitates were collected by filtration and washed with 0.1 M HCl and water and then dried. Purification by column chromatography afforded sulfonamides. Their structures were identified by spectroscopic techniques.

2.2 Synthesis of metal complexes

Sulfonamide (1.0 mmol) was dissolved in 30 mL of methanol. After stirring at 80°C for 0.5 h, a solution 1.0 mmol of metal salts (Cu(II), Zn(II), Ni(II) or Mn(II)) in 5 mL of methanol, was added. The solution was added 15 mL of methanol and stirred for additional 0.5 h, then added the synthesized sulfonamide (1.0 mmol) or 2-, 3-, 4-pyridine dissolved in 5 mL of methanol. The solution was added 15 mL of methanol and stirred for 0.5 h until the reaction was completed, then allowed to cool. The metal complex product was collected by filtration and analyzed by spectroscopic data.

3. Physical properties and structure determination of synthetic compounds.

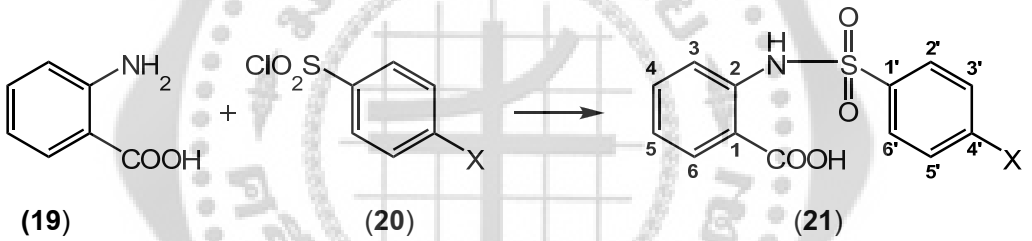
Synthetic compounds were determined for their melting points. Their structures were deduced by spectroscopic techniques such as infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (NMR) and magnetic susceptibility.

CHAPTER 4

RESULTS AND DISCUSSION

1. Synthesis of anthranilic acid sulfonamides and metal complexes

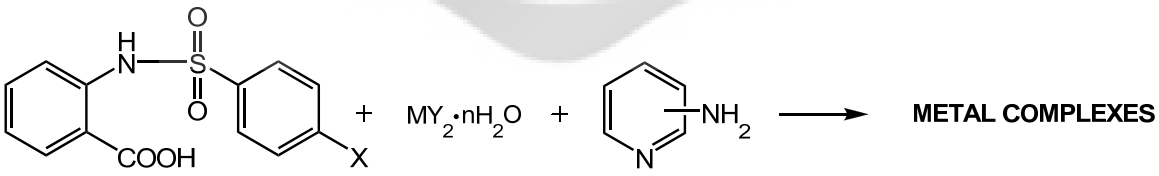
Sulfonamides (**21**) were synthesized (in 80-98%) from the reaction of anthranilic acid (**19**) and arenesulfonyl chloride (**20**). Each sulfonamide reacted with itself and/or diferrent sulfonamides (**21**) or 2-, 3-, 4-aminopyridines and metal salts ($\mathbf{MY_2 \cdot nH_2O}$) to form metal complexes (**L1-M-L2**) in 1 : 1 : 1 mole ratio as given in Scheme 1. Their spectral data are summarized in section 2 as well as physical properties and percentage yield of the synthetic compounds as shown in Tables 4 and 5.



(**19**) (**20**) (**21**)

21a; **X** = NO_2 **21c**; **X** = CH_3

21b; **X** = OCH_3 **21d**; **X** =Cl



(**21**) (**22**) (**L1-M-L2**)

M = Cu(II), Zn(II), Ni(II), Mn(II)

Y = CH_3COO, Cl

Scheme 1 Synthesis of sulfonamide (**21**)

2. Spectroscopic data of synthesis compounds

2.1 Sulfonamides

2.1.1 2-(4'-Nitrophenylsulfonamido)benzoic acid (**21a**) (**SA.01**)

R_f 0.45 (20 % EtOAc : hexane)

IR ν_{max}^{KBr} cm^{-1} :

3449(m, br) ν(O–H), 1393(m, sh) δ(O–H)

3196(m, sh) ν(N–H), 1582(m), 758(s) δ(N–H)

1665(s) ν(C=O), 1086(s) ν(C–O)

1264(s) ν(C–N), 926(s) ν(S–N)

1318(m), 1162(vs) $\nu(SO_2)$

1531(vs), 1349(s) $\nu(NO_2)$

^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm)

7.14 (br t, *J* = 7.1 Hz, 1H, H-3)

7.46 (br d, *J* =7.7 Hz, 1H, H-4)

7.54 (br t, *J* = 7.6 Hz, 1H, H-5)

7.88 (dd, *J* = 7.4 Hz, 1H, H-2)

8.06 (d, *J* = 8.7 Hz, 1H, H-3', H-5')

8.34 (d, *J* = 8.7 Hz, 2H, H-2', H-6')

2.1.2 2-(4'-Methoxyphenylsulfonamido)benzoic acid (**21b**) (**SA.02**)

R_f 0.43 (20 % EtOAc : hexane)

IR ν_{max}^{KBr} cm^{-1} :

3492(m, br) ν(O–H), 1389(s) δ(O–H)

3202(s, sh) ν(N–H)

1581(s), 754(s) δ(N–H)

1678(s) ν(C=O)

1092(s), 1022(s) ν(C–O)

1261(s) ν(C–N)

926(s) ν(S–N)

1344(m), 1160(s) $\nu(SO_2)$

^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm)

3.70 (s, 3H, OCH_3)

6.90 (t, *J* = 7.4 Hz, 1H, H-5)

6.96 (d, *J* = 8.7 Hz, 2H, H-3', H-5')

7.22 (t, *J* = 7.6 Hz, 1H, H-4)

7.32 (d, *J* = 8.1 Hz, 1H, H-3)

7.76 (d, *J* = 8.7 Hz, 2H, H-2', H-6')

7.78 (d, *J* = 7.7 Hz, 1H, H-6)

14.44 (br s, 1H, NH)

2.1.3 2-(4'-Methylphenylsulfonamido)benzoic acid (**21c**) (**SA.03**)

R_f 0.47 (20 % EtOAc : hexane)

IR ν_{max}^{KBr} cm^{-1} :

3449(w, br) ν(O–H), 1389(m) δ(O–H)

3201(m, sh) ν(N–H), 1585(m), 754(s) δ(N–H)

1675(s) ν(C=O), 1089(s) ν(C–O)

1258(s) ν(C–N), 922(s) ν(S–N)

1342(s), 1162(s) ν(SO_2)

^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm)

2.25 (s, 3H, CH_3)

6.98 (br t, *J* = 7.3 Hz, 1H, H-5)

7.28 (d, *J* = 8.0 Hz, 2H, H-3', H-5')

7.34 (br t, *J* = 7.3 Hz, 1H, H-4)

7.39 (br d, *J* = 7.9 Hz, 1H, H-3)

7.62 (d, *J* = 8.0 Hz, 2H, H-2', H-6')

7.82 (br d, *J* = 7.6 Hz, 1H, H-6)

2.1.4 2-(4'-Chlorophenylsulfonamido)benzoic acid (**21d**) (**SA.04**)

R_f 0.50 (20 % EtOAc : hexane)

IR ν_{max}^{KBr} cm^{-1} :

3442(w, br) ν(O–H), 1380(m) δ(O–H)

3188(w, sh) ν(N–H), 1585(s), 753(s) δ(N–H)

1662(s) ν(C=O), 1093(s) ν(C–O)

1261(m) ν(C–N), 929(s) ν(S–N)

1342(s), 1164(s) $\nu(SO_2)$

^{1}H NMR (300 MHz, DMSO-d_6) : δ (ppm)

7.14 (br t, *J* = 7.1 Hz, 1H, H-5)

7.47 (br d, *J* = 7.8 Hz, 1H, H-4)

7.55 (br td, *J* = 7.7 Hz, 1H, H-3)

7.62 (d, *J* = 8.6 Hz, 2H, H-3', H-5')

7.81 (d, *J* = 8.6 Hz, 2H, H-2', H-6')

7.88 (dd, *J* = 7.3 Hz, 1H, H-6)

2.2 Copper complexes of Sulfonamides and 2-, 3-, 4-Aminopyridines

2.2.1 SA.01 + Cu(II) + SA.01 (**SACu1**)

IR ν_{max}^{KBr} cm^{-1} :

3475(m, br) ν(O–H), 1394(s, sh) δ(O–H)

1091(m, sh) ν(C–O), 1276(s) ν(C–N), 945(s) ν(S–N)

1314(m), 1164(vs) $\nu(SO_2)$

1531(s), 1394(vs) $\nu(NO_2)$

μ_{eff} 0.82 B.M.

2.2.2 SA.02 + Cu(II) + SA.02 (**SACu2**)

IR ν_{max}^{KBr} cm^{-1} :

3471(m, br) ν(O–H), 1397(s) δ(O–H)

1096(s), 1025(m) ν(C–O), 1264(s) ν(C–N)

931(s, br) ν(S–N), 1330(m, br), 1153(s) $\nu(SO_2)$

μ_{eff} 0.79 B.M.

2.2.3 SA.03 + Cu(II) + SA.03 (**SACu3**)

IR ν_{max}^{KBr} cm^{-1} :

3554(s, sh), 3493(m, sh) ν(O–H), 1394(vs) δ(O–H)

1090(s) ν(C–O), 1268(s) ν(C–N), 927(s) ν(S–N)

1331(m), 1169(s) $\nu(SO_2)$

μ_{eff} 0.93 B.M.

2.2.4 SA.04 + Cu(II) + SA.04 (**SACu4**)

IR ν_{max}^{KBr} cm^{-1} :

3465(m, br) ν(O–H), 1396(vs) δ(O–H)

1095(s) ν(C–O), 1279(s) ν(C–N), 937(s, br) ν(S–N)

1335(m), 1159(s) $\nu(SO_2)$

μ_{eff} 0.69 B.M.

2.2.5 SA.01 + Cu(II) + SA.02 (**SACu5**)

IR ν_{max}^{KBr} cm^{-1} :

3448(s, br) ν(O–H), 1396(vs) δ(O–H)

1093(s), 1024(w) ν(C–O)

938(s, br) ν(S–N), 1274(m) ν(C–N)

1161(s) $\nu(SO_2)$, 1534(s), 1350(s) $\nu(NO_2)$

μ_{eff} 0.80 B.M.

2.2.6 SA.01 + Cu(II) + SA.03 (**SACu6**)

IR ν_{max}^{KBr} cm^{-1} :

3449(s, br) ν(O–H), 1396(vs) δ(O–H)

1091(s) ν(C–O), 1274(m) ν(C–N), 941(m, br) ν(S–N)

1163(vs) $\nu(SO_2)$, 1534(s), 1350(s) $\nu(NO_2)$

μ_{eff} 0.80 B.M.

2.2.7 SA.01 + Cu(II) + SA.04 (**SACu7**)

IR ν_{max}^{KBr} cm^{-1} :

3450(s, br) ν(O–H), 1396(vs) δ(O–H)

1093(s) ν(C–O), 1274(s) ν(C–N), 941(m, br) ν(S–N)

1161(vs) ν(SO_2), 1534(s), 1350(s) ν(NO_2)

μ_{eff} 0.84 B.M.

2.2.8 SA.02 + Cu(II) + SA.03 (**SACu8**)

IR ν_{max}^{KBr} cm^{-1} :

3449(s, br) ν(O–H), 1396(s) δ(O–H)

1093(m), 1024(vw) ν(C–O)

1267(m) ν(C–N), 934(w, br) ν(S–N)

1156(s) ν(SO_2)

μ_{eff} 0.54 B.M.

2.2.9 SA.02 + Cu(II) + SA.04 (**SACu9**)

IR ν_{max}^{KBr} cm^{-1} :

3449(m, br) ν(O–H), 1396(vs) δ(O–H)

1093(s), 1024(w) ν(C–O)

1274(s) ν(C–N), 938(m, br) ν(S–N)

1332(w), 1156(vs) ν(SO_2)

μ_{eff} 0.82 B.M.

2.2.10 SA.03 + Cu(II) + SA.04 (**SACu10**)

IR ν_{max}^{KBr} cm^{-1} :

3448(s, br) ν(O–H), 1396(vs) δ(O–H)

3181(w, br) ν(N–H), 1094(s) ν(C–O), 1275(s) ν(C–N)

936(s, br) ν(S–N), 1334(m), 1158(vs) ν(SO_2)

μ_{eff} 0.82 B.M.

2.2.11 SA.01 + Cu(II) + 2AP (**SACu11**)

IR ν_{max}^{KBr} cm^{-1} :

3460(s, br) ν(O–H), 1394(s) δ(O–H)

3101(w, sh) ν(N–H), 773(s) δ(N–H)

1090(m) ν(C–O), 1276(m) ν(C–N), 943(s, br) ν(S–N)

1317(s), 1164(s) $\nu(SO_2)$, 1537(s), 1349(s) $\nu(NO_2)$

μ_{eff} 0.69 B.M.

2.2.12 SA.01 + Cu(II) + 3AP (**SACu12**)

IR ν_{max}^{KBr} cm^{-1} :

3474(s, br) ν(O–H), 1394(s) δ(O–H)

3101(w, sh) ν(N–H), 773(s) δ(N–H)

1090(s) ν(C–O), 1276(s) ν(C–N), 944(s, br) ν(S–N)

1314(w), 1164(s) $\nu(SO_2)$, 1538(s), 1349(s) $\nu(NO_2)$

μ_{eff} 0.69 B.M.

2.2.13 SA.01 + Cu(II) + 4AP (**SACu13**)

IR ν_{max}^{KBr} cm^{-1} :

3474(s, br) ν(O–H), 1394(vs) δ(O–H)

3100(m, sh) ν(N–H), 773(s) δ(N–H)

1091(s) ν(C–O), 1276(s) ν(C–N), 945(s, br) ν(S–N)

1314(m), 1165(vs) $\nu(SO_2)$, 1531(s), 1349(s) $\nu(NO_2)$

μ_{eff} 0.69 B.M.

2.2.14 SA.02 + Cu(II) + 2AP (**SACu14**)

IR ν_{max}^{KBr} cm^{-1} :

3449(s, br) ν(O–H), 1396(vs) δ(O–H)

3181(m, br) ν(N–H), 1560(s), 767(s) δ(N–H)

1095(s), 1024(s) ν(C–O) 1264(s) ν(C–N), 934(s, br) ν(S–N)

1332(m), 1154(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.2.15 SA.02 + Cu(II) + 3AP (**SACu15**)

IR ν_{max}^{KBr} cm^{-1} :

3449(m, br) ν(O–H), 1396(s, sh) δ(O–H)

3188(m, br) ν(N–H), 764(s) δ(N–H), 1093(s), 1024(s) ν(C–O)

1263(s) ν(C–N), 934(m, br) ν(S–N), 1154(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.2.16 SA.02 + Cu(II) + 4AP (**SACu16**)

IR ν_{max}^{KBr} cm^{-1} :

3448(s, br) ν(O–H), 1396(vs) δ(O–H)

3196(m, br) ν(N–H), 768(s) δ(N–H)

1095(s), 1024(s) ν(C–O), 1264(s) ν(C–N)

932(s, br) ν(S–N), 1153(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.2.17 SA.03 + Cu(II) + 2AP (**SACu17**)

IR ν_{max}^{KBr} cm^{-1} :

3555(s, br) ν(O–H), 1394(vs) δ(O–H)

3492(s, br) ν(N–H), 768(s) δ(N–H)

1089(s) ν(C–O), 1268(s) ν(C–N)

927(s) ν(S–N), 1170(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.2.18 SA.03 + Cu(II) + 3AP (**SACu18**)

IR ν_{max}^{KBr} cm^{-1} :

3555(s, br) ν(O–H), 1394(vs) δ(O–H)

3130(m, br) ν(N–H), 768(s, sh) δ(N–H)

1089(s) ν(C–O), 1267(s) ν(C–N)

927(s, sh) ν(S–N), 1170(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.2.19 SA.03 + Cu(II) + 4AP (**SACu19**)

IR ν_{max}^{KBr} cm^{-1} :

3555(s, br) ν(O–H), 1394(vs) δ(O–H)

3492(s, br) ν(N–H), 1598(s) δ(N–H), 1090(s, sh) ν(C–O)

1268(s, sh) ν(C–N), 927(s, sh) ν(S–N)

1170(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.2.20 SA.04 + Cu(II) + 2AP (**SACu20**)

IR ν_{max}^{KBr} cm^{-1} :

3464(s, br) ν(O–H), 1396(vs) δ(O–H)

3174(m, br) ν(N-H), 754(s) δ(N-H), 1095(vs) ν(C–O)

1280(s) ν(C–N), 938(s, br) ν(S–N)

1159(vs) $\nu(SO_2)$

μ_{eff} 0.72 B.M.

2.2.21 SA.04 + Cu(II) + 3AP (**SACu21**)

IR ν_{max}^{KBr} cm^{-1} :

3473(s, br) ν(O–H), 1396(vs) δ(O–H)

3181(m, br) ν(N-H), 754(s) δ(N-H), 1095(vs) ν(C–O)

1280(s) ν(C–N), 939(s, br) ν(S–N)

1159(vs) $\nu(SO_2)$

μ_{eff} 0.72 B.M.

2.2.22 SA.04 + Cu(II) + 4AP (**SACu22**)

IR ν_{max}^{KBr} cm^{-1} :

3464(s, br) ν(O–H), 1396(vs) δ(O–H)

3156(m, br) ν(N-H), 754(s) δ(N-H), 1095(s, sh) ν(C–O)

1280(s, sh) ν(C–N), 938(s) ν(S–N)

1159(vs) $\nu(SO_2)$

μ_{eff} 0.72 B.M.

2.3 Zinc complexes of Sulfonamides and 2-, 3-, 4-Aminopyridines

2.3.1 SA.01 + Zn(II) + SA.01 (**SAZn1**)

IR ν_{max}^{KBr} cm^{-1} :

3449(m, br) ν(O–H), 1382(s) δ(O–H)

1709(vs) ν(C=O), 1082(s) ν(C–O)

1249(m) ν(C–N), 961(m) ν(S–N)

1306(m), 1183(vs) $\nu(SO_2)$

1534(vs), 1352(s) $\nu(NO_2)$

μ_{eff} 0.82 B.M.

2.3.2 SA.02 + Zn(II) + SA.02 (**SAZn2**)

IR ν_{max}^{KBr} cm^{-1} :

3449(m, br) ν(O–H), 1397(s) δ(O–H)

1095(s), 1025(s) ν(C–O), 1265(s) ν(C–N)

935(s) ν(S–N), 1326(m)

1153(vs) $\nu(SO_2)$

μ_{eff} 0.79 B.M.

2.3.3 SA.03 + Zn(II) + SA.03 (**SAZn3**)

No reaction

2.3.4 SA.04 + Zn(II) + SA.04 (**SAZn4**)

IR ν_{max}^{KBr} cm^{-1} :

3449(w, br) ν(O–H), 1396(s) δ(O–H)

1095(s) ν(C–O) 1279(m) ν(C–N)

941(m, br) ν(S–N)

1158(s) $\nu(SO_2)$

μ_{eff} 0.86 B.M.

2.3.5 SA.01 + Zn(II) + SA.02 (**SAZn5**)

IR ν_{max}^{KBr} cm^{-1} :

3446(m, br) ν(O–H), 1376(m) δ(O–H)

1717(s) ν(C=O), 1082(s) ν(C–O)

1249(m) ν(C–N), 963(s) ν(S–N)

1305(m), 1183(s) $\nu(SO_2)$, 1541(vs), 1351(s) $\nu(NO_2)$

μ_{eff} 0.81 B.M.

2.3.6 SA.01 + Zn(II) + SA.03 (**SAZn6**)

IR ν_{max}^{KBr} cm^{-1} :

3450(s, br) ν(O–H), 1374(m) δ(O–H)

1708(s) ν(C=O), 1082(s) ν(C–O)

1249(m) ν(C–N), 963(s) ν(S–N)

1306(m), 1183(vs) $\nu(SO_2)$

1541(vs), 1351(s) $\nu(NO_2)$

μ_{eff} 0.81 B.M.

2.3.7 SA.01 + Zn(II) + SA.04 (**SAZn7**)

IR ν_{max}^{KBr} cm^{-1} :

3446(m, br) ν(O–H), 1382(s) δ(O–H)

1709(vs) ν(C=O), 1082(s) ν(C–O)

1249(s) ν(C–N), 960(s) ν(S–N)

1306(s), 1183(vs) $\nu(SO_2)$

1540(vs), 1352(s) $\nu(NO_2)$

μ_{eff} 0.84 B.M.

2.3.8 SA.02 + Zn(II) + SA.03 (**SAZn8**)

No reaction

2.3.9 SA.02 + Zn(II) + SA.04 (**SAZn9**)

No reaction

2.3.10 SA.03 + Zn(II) + SA.04 (**SAZn10**)

IR ν_{max}^{KBr} cm^{-1} :

3446(m, br) ν(O–H), 1375(s) δ(O–H)

1702(s) ν(C=O), 1080(s) ν(C–O)

1249(s) ν(C–N), 960(m) ν(S–N), 1175(vs) $\nu(SO_2)$

μ_{eff} 1.08 B.M.

2.3.11 SA.01 + Zn(II) + 2AP (**SAZn11**)

IR ν_{max}^{KBr} cm^{-1} :

3447(w, br) ν(O–H), 1373(m) δ(O–H)

1718(s) ν(C=O), 1084(m) ν(C–O)

1274(m, br) ν(C–N), 961(w, br) ν(S–N)

1306(m, br), 1183(s) $\nu(SO_2)$, 1542(vs), 1373(m) $\nu(NO_2)$

μ_{eff} 0.69 B.M.

2.3.12 SA.01 + Zn(II) + 3AP (**SAZn12**)

IR ν_{max}^{KBr} cm^{-1} :

3463(s, br) ν(O–H), 1410(s) δ(O–H)

3372(s, br) ν(N–H), 1577(m), 737(s) δ(N–H)

1087(s) ν(C–O), 1273(s) ν(C–N) 972(s) ν(S–N)

1145(vs) $\nu(SO_2)$, 1524(vs), 1352(s) $\nu(NO_2)$

μ_{eff} 0.69 B.M.

2.3.13 SA.01 + Zn(II) + 4AP (**SAZn13**)

IR ν_{max}^{KBr} cm^{-1} :

3463(s, br) ν(O–H), 1404(s, br) δ(O–H)

3363(s, br) ν(N–H), 1576(m), 738(s, br) δ(N–H)

1087(s) ν(C–O), 1262(m), 1281(m, br) ν(C–N), 968(s) ν(S–N)

1147(s, sh) $\nu(SO_2)$, 1526(vs), 1352(s) $\nu(NO_2)$

μ_{eff} 0.69 B.M.

2.3.14 SA.02 + Zn(II) + 2AP (**SAZn14**)

IR ν_{max}^{KBr} cm^{-1} :

3442(w, br) ν(O–H), 1374(s) δ(O–H)

1560(s, sh), 777(m) δ(N–H), 1082(s), 1018(s) ν(C–O)

1263(s) ν(C–N), 955(m) ν(S–N)

1164(s) $\nu(SO_2)$

μ_{eff} 0.89 B.M.

2.3.15 SA.02 + Zn(II) + 3AP (**SAZn15**)

IR ν_{max}^{KBr} cm^{-1} :

3466(m, br) ν(O–H), 1389(s) δ(O–H)

3376(s, br) ν(N–H), 1597(s), 763(s) δ(N–H)

1094(s), 1026(m) ν(C–O), 1267(s) ν(C–N)

940(m, br) ν(S–N), 1155(vs) $\nu(SO_2)$

μ_{eff} 0.75 B.M.

2.3.16 SA.02 + Zn(II) + 4AP (**SAZn16**)

IR ν_{max}^{KBr} cm^{-1} :

3442(s, br) ν(O–H), 1374(s) δ(O–H)

830(s) δ(N–H), 1699(s) ν(C=O)

1080(s), 1020(s) ν(C–O), 1265(s) ν(C–N)

960(m) ν(S–N), 1164(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.3.17 SA.03 + Zn(II) + 2AP (**SAZn17**)

IR ν_{max}^{KBr} cm^{-1} :

3444(w, br) ν(O–H), 1396(s) δ(O–H)

1560(s), 718(m) δ(N–H), 1718(s) ν(C=O)

1081(m) ν(C–O), 1252(m) ν(C–N)

959(m, br) ν(S–N), 1174(s) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.3.18 SA.03 + Zn(II) + 3AP (**SAZn18**)

IR ν_{max}^{KBr} cm^{-1} :

3444(m, br) ν(O–H), 1376(s) δ(O–H)

1560(s, sh) δ(N–H)

1702(s) ν(C=O), 1080(s) ν(C–O)

1249(m) ν(C–N), 960(m, br) ν(S–N)

1638 (m, sh) ν(C=N), 1174(s) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.3.19 SA.03 + Zn(II) + 4AP (**SAZn19**)

No reaction

2.3.20 SA.04 + Zn(II) + 2AP (**SAZn20**)

No reaction

2.3.21 SA.04 + Zn(II) + 3AP (**SAZn21**)

No reaction

2.3.22 SA.04 + Zn(II) + 4AP (**SAZn22**)

IR ν_{max}^{KBr} cm^{-1} :

3442(m, br) ν(O–H), 1374(s) δ(O–H)

1560(m, sh) δ(N–H),

1705(s) ν(C=O), 1080(s) ν(C–O)

1306(s), 1249(s) ν(C–N), 960(s, br) ν(S–N)

1654 (m, sh) ν(C=N), 1174(s) $\nu(SO_2)$

μ_{eff} 0.72 B.M.

2.4 Nickel complexes of Sulfonamides and 2-, 3-, 4-Aminopyridines

2.4.1 SA.01 + Ni(II) + SA.01 (**SANi1**)

IR ν_{max}^{KBr} cm^{-1} :

3448(m, br) ν(O–H), 1374(m, sh) δ(O–H)

1709(vs) ν(C=O), 1092(s) ν(C–O)

1249(m) ν(C–N), 958(m) ν(S–N)

1306(s), 1183(vs) $\nu(SO_2)$

1540(vs), 1351(s) $\nu(NO_2)$

μ_{eff} 0.82 B.M.

2.4.2 SA.02 + Ni(II) + SA.02 (**SANi2**)

No reaction

2.4.3 SA.03 + Ni(II) + SA.03 (**SANi3**)

IR ν_{max}^{KBr} cm^{-1} :

3450(w, br) ν(O–H), 1375(m) δ(O–H)

1702(vs) ν(C=O), 1083(s) ν(C–O)

1248(s) ν(C–N), 959(m) ν(S–N)

1175(s) $\nu(SO_2)$

μ_{eff} 0.79 B.M.

2.4.4 SA.04 + Ni(II) + SA.04 (**SANi4**)

IR ν_{max}^{KBr} cm^{-1} :

3450(w, br) ν(O–H), 1396(s) δ(O–H)

1095(s) ν(C–O), 1276(m) ν(C–N)

947(m) ν(S–N)

1339(m), 1157(s) $\nu(SO_2)$

μ_{eff} 0.90 B.M.

2.4.5 SA.01 + Ni(II) + SA.02 (**SANi5**)

IR ν_{max}^{KBr} cm^{-1} :

3446(m, br) ν(O–H), 1375(s) δ(O–H)

1717(s) ν(C=O), 1081(s) ν(C–O)

1249(s) ν(C–N), 959(m) ν(S–N)

1306(s), 1181(s) $\nu(SO_2)$, 1542(vs), 1376(s) $\nu(NO_2)$

μ_{eff} 0.80 B.M.

2.4.6 SA.01 + Ni(II) + SA.03 (**SANi6**)

IR ν_{max}^{KBr} cm^{-1} :

3446(m, br) ν(O–H), 1375(s) δ(O–H)

1717(s) ν(C=O), 1081(s) ν(C–O)

1249(s) ν(C–N), 959(m) ν(S–N)

1306(s), 1181(s) $\nu(SO_2)$, 1542(vs), 1376(s) $\nu(NO_2)$

μ_{eff} 0.80 B.M.

2.4.7 SA.01 + Ni(II) + SA.04 (**SANi7**)

IR ν_{max}^{KBr} cm^{-1} :

3447(s, br) ν(O–H), 1388(s, br) δ(O–H)

1094(s, sh) ν(C–O), 1274(s) ν(C–N), 950(s, br) ν(S–N)

1319(m, br), 1158(vs) $\nu(SO_2)$

1540(s, sh), 1351(vm) $\nu(NO_2)$

μ_{eff} 0.93 B.M.

2.4.8 SA.02 + Ni(II) + SA.03 (**SANi8**)

IR ν_{max}^{KBr} cm^{-1} :

3445(m, br) ν(O–H), 1375(s) δ(O–H)

1702(s) ν(C=O), 1079(s) ν(C–O)

1274(m) ν(C–N), 959(w) ν(S–N)

1174(s) $\nu(SO_2)$

μ_{eff} 0.79 B.M.

2.4.9 SA.02 + Ni(II) + SA.04 (**SANi9**)

IR ν_{max}^{KBr} cm^{-1} :

3446(m, br) ν(O–H), 1396(s) δ(O–H)

1095(s) ν(C–O), 1269(m) ν(C–N), 949(w, br) ν(S–N)

1340(m, sh), 1154(s) $\nu(SO_2)$

μ_{eff} 1.16 B.M.

2.4.10 SA.03 + Ni(II) + SA.04 (**SANi10**)

IR ν_{max}^{KBr} cm^{-1} :

3447(m, br) ν(O–H), 1374(s) δ(O–H)

1702(s) ν(C=O), 1080(s) ν(C–O)

1246(m) ν(C–N), 963(m) ν(S–N), 1175(s) $\nu(SO_2)$

μ_{eff} 0.82 B.M.

2.4.11 SA.01 + Ni(II) + 2AP (**SANi11**)

IR ν_{max}^{KBr} cm^{-1} :

3449(m, br) ν(O–H), 1374(s, br) δ(O–H)

1560(m, sh), 742(s, sh) δ(N–H)

1717(s) ν(C=O), 1082(s) ν(C–O)

1249(m) ν(C–N), 960(m, br) ν(S–N)

1183(vs) $\nu(SO_2)$, 1541(vs) $\nu(NO_2)$

μ_{eff} 0.69 B.M.

2.4.12 SA.01 + Ni(II) + 3AP (**SANi12**)

IR ν_{max}^{KBr} cm^{-1} :

3442(m, br) ν(O–H), 1374(s) δ(O–H)

3113(s, br) ν(N–H)

1716(s) ν(C=O), 1082(s) ν(C–O)

1249(m) ν(C–N), 960(s) ν(S–N)

1183(vs) $\nu(SO_2)$, 1540(vs), 1352(s) $\nu(NO_2)$

μ_{eff} 0.69 B.M.

2.4.13 SA.01 + Ni(II) + 4AP (**SANi13**)

IR ν_{max}^{KBr} cm^{-1} :

3442(w, br) ν(O–H), 1394(vs) δ(O–H)

3100(m, sh) ν(N–H), 773(s) δ(N–H)

1716(s) ν(C=O), 1082(s) ν(C–O)

1249(m) ν(C–N), 960(s) ν(S–N)

1314(m), 1165(vs) $\nu(SO_2)$, 1531(s), 1349(s) $\nu(NO_2)$

μ_{eff} 0.69 B.M.

2.4.14 SA.02 + Ni(II) + 2AP (**SANi14**)

IR ν_{max}^{KBr} cm^{-1} :

3448(m, br) ν(O–H), 1374(m, sh) δ(O–H)

1596(vs), 775(w, sh) δ(N–H)

1701(vs) ν(C=O), 1080(s), 1019(s) ν(C–O)

1264(s) ν(C–N), 960(s) ν(S–N), 1164(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.4.15 SA.02 + Ni(II) + 3AP (**SANi15**)

IR ν_{max}^{KBr} cm^{-1} :

3446(s, br) ν(O–H), 1374(s) δ(O–H)

1596(s), 776(m) δ(N–H)

1702(s) ν(C=O), 1082(s), 1019(s) ν(C–O)

1263(s) ν(C–N), 949(m) ν(S–N), 1164(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.4.16 SA.02 + Ni(II) + 4AP (**SANi16**)

IR ν_{max}^{KBr} cm^{-1} :

3448(s, br) ν(O–H), 1373(s) δ(O–H)

831(s) δ(N–H), 1699(vs) ν(C=O), 1081(s), 1019(s) ν(C–O)

1263(s) ν(C–N), 960(s) ν(S–N), 1164(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.4.17 SA.03 + Ni(II) + 2AP (**SANi17**)

IR ν_{max}^{KBr} cm^{-1} :

3449(m, br) ν(O–H), 1375(s) δ(O–H)

723(s) δ(N–H), 1703(vs) ν(C=O), 1081(s) ν(C–O)

1249(s) ν(C–N), 1174(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.4.18 SA.03 + Ni(II) + 3AP (**SANi18**)

IR ν_{max}^{KBr} cm^{-1} :

3428(m, br) ν(O–H), 1375(s) δ(O–H)

722(m) δ(N–H), 1702(s) ν(C=O), 1080(s) ν(C–O)

1248(s) ν(C–N), 959(m, br) ν(S–N), 1174(s) $\nu(SO_2)$

μ_{eff} 0.82 B.M.

2.4.19 SA.03 + Ni(II) + 4AP (**SANi19**)

IR ν_{max}^{KBr} cm^{-1} :

3447(m, br) ν(O–H), 1376(s) δ(O–H)

723(s) δ(N–H), 1702(s) ν(C=O), 1080(s) ν(C–O)

1250(m), 1306(s) ν(C–N), 961(m, br) ν(S–N)

1174(s) $\nu(SO_2)$

μ_{eff} 0.79 B.M.

2.4.20 SA.04 + Ni(II) + 2AP (**SANi20**)

No reaction

2.4.21 SA.04 + Ni(II) + 3AP (**SANi21**)

No reaction

2.4.22 SA.04 + Ni(II) + 4AP (**SANi22**)

No reaction

2.5 Manganese complexes of Sulfonamides and 2-, 3-, 4-Aminopyridines

2.5.1 SA.01 + Mn(II) + SA.01 (**SAMn1**)

IR ν_{max}^{KBr} cm^{-1} :

3448(m, br) ν(O–H), 1374(m, sh) δ(O–H)

1708(vs) ν(C=O), 1082(m, sh) ν(C–O)

1248(m) ν(C–N), 960(m) ν(S–N)

1306(s), 1183(vs) $\nu(SO_2)$

1541(vs), 1353(s) $\nu(NO_2)$

μ_{eff} 0.82 B.M.

2.5.2 SA.02 + Mn(II) + SA.02 (**SAMn2**)

No reaction

2.5.3 SA.03 + Mn(II) + SA.03 (**SAMn3**)

IR ν_{max}^{KBr} cm^{-1} :

3448(w, br) ν(O–H), 1375(s) δ(O–H)

1702(vs) ν(C=O), 1080(s) ν(C–O)

1249(s) ν(C–N), 960(m) ν(S–N)

1305(s), 1174(vs) $\nu(SO_2)$

μ_{eff} 0.79 B.M.

2.5.4 SA.04 + Mn(II) + SA.04 (**SAMn4**)

No reaction

2.5.5 SA.01 + Mn(II) + SA.02 (**SAMn5**)

IR ν_{max}^{KBr} cm^{-1} :

3448(s, br) ν(O–H), 1374(s) δ(O–H)

1707(s) ν(C=O), 1082(s) ν(C–O)

1250(s) ν(C–N), 958(s) ν(S–N)

1306(s), 1181(vs) $\nu(SO_2)$

1541(vs), 1353(m) $\nu(NO_2)$

μ_{eff} 0.80 B.M.

2.5.6 SA.01 + Mn(II) + SA.03 (**SAMn6**)

IR ν_{max}^{KBr} cm^{-1} :

3448(s, br) ν(O–H), 1374(s) δ(O–H)

1707(s) ν(C=O), 1082(s) ν(C–O)

1250(s) ν(C–N), 958(s) ν(S–N)

1306(s), 1181(vs) $\nu(SO_2)$, 1541(vs), 1353(m) $\nu(NO_2)$

μ_{eff} 0.73 B.M.

2.5.7 SA.01 + Mn(II) + SA.04 (**SAMn7**)

IR ν_{max}^{KBr} cm^{-1} :

3449(m, br) ν(O–H), 1375(s) δ(O–H)

1817(s) ν(C=O), 1081(s) ν(C–O)

1256(m) ν(C–N), 960(w, br) ν(S–N)

1307(m), 1183(vs) $\nu(SO_2)$, 1541(vs), 1352(s) $\nu(NO_2)$

μ_{eff} 0.84 B.M.

2.5.8 SA.02 + Mn(II) + SA.03 (**SAMn8**)

IR ν_{max}^{KBr} cm^{-1} :

3445(w, br) ν(O–H), 1375(s) δ(O–H)

1702(s) ν(C=O), 1082(m) ν(C–O)

1246(m) ν(C–N), 959(w) ν(S–N), 1175(s) $\nu(SO_2)$

μ_{eff} 0.79 B.M.

2.5.9 SA.02 + Mn(II) + SA.04 (**SAMn9**)

IR ν_{max}^{KBr} cm^{-1} :

3446(m, br) ν(O–H), 1374(s) δ(O–H)

1699(s) ν(C=O), 1082(s), 1018(m) ν(C–O)

1265(s) ν(C–N), 959(w) ν(S–N), 1164(s) $\nu(SO_2)$

μ_{eff} 0.82 B.M.

2.5.10 SA.03 + Mn(II) + SA.04 (**SAMn10**)

No reaction

2.5.11 SA.01 + Mn(II) + 2AP (**SAMn11**)

No reaction

2.5.12 SA.01 + Mn(II) + 3AP (**SAMn12**)

IR ν_{max}^{KBr} cm^{-1} :

3446(m, br) ν(O–H), 1374(m, sh) δ(O–H)

742(s) δ(N–H), 1249(s) ν(C–N), 960(m, br) ν(S–N)

1716(s) ν(C=O), 1082(s) ν(C–O)

1183(vs) $\nu(SO_2)$

1540(vs), 1351(m, br) $\nu(NO_2)$

μ_{eff} 0.69 B.M.

2.5.13 SA.01 + Mn(II) + 4AP (**SAMn13**)

No reaction

2.5.14 SA.02 + Mn(II) + 2AP (**SAMn14**)

IR ν_{max}^{KBr} cm^{-1} :

3447(w, br) ν(O–H), 1374(s) δ(O–H)

1560(s), 755(w, sh) δ(N–H)

1698(vs) ν(C=O), 1082(s), 1016(s) ν(C–O)

1263(s) ν(C–N), 949(m) ν(S–N), 1164(s) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.5.15 SA.02 + Mn(II) + 3AP (**SAMn15**)

IR ν_{max}^{KBr} cm^{-1} :

1397(m, sh) δ(O–H)

1699(s, sh) ν(C=O), 1080(m), 1020(w) ν(C–O)

1263(m) ν(C–N), 1162(m) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.5.16 SA.02 + Mn(II) + 4AP (**SAMn16**)

IR ν_{max}^{KBr} cm^{-1} :

3448(w, br) ν(O–H), 1374(s) δ(O–H)

1559(s), 833(s) δ(N–H)

1699(s) ν(C=O), 1081(s), 1020(s) ν(C–O)

1262(s) ν(C–N), 1654(s) ν(C=N), 957(m) ν(S–N)

1164(s) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.5.17 SA.03 + Mn(II) + 2AP (**SAMn17**)

IR ν_{max}^{KBr} cm^{-1} :

3448(w, br) ν(O–H), 1396(s) δ(O–H)

1560(s), 718(m) δ(N–H)

1718(s) ν(C=O), 1081(m) ν(C–O)

1252(m) ν(C–N), 959(m, br) ν(S–N)

1174(s) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.5.18 SA.03 + Mn(II) + 3AP (**SAMn18**)

IR ν_{max}^{KBr} cm^{-1} :

3444(m, br) ν(O–H), 1376(s) δ(O–H)

1560(s, sh), 723(s) δ(N–H)

1702(s) ν(C=O), 1080(s) ν(C–O)

1249(m) ν(C–N), 960(m, br) ν(S–N)

1174(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.5.19 SA.03 + Mn(II) + 4AP (**SAMn19**)

IR ν_{max}^{KBr} cm^{-1} :

3449(m, br) ν(O–H), 1375(m, br) δ(O–H)

1560(m, sh), 723(s) δ(N–H)

1702(s) ν(C=O), 1080(s) ν(C–O)

1250(m) ν(C–N), 1654(s, sh) ν(C=N), 961(m, sh) ν(S–N)

1174(vs) $\nu(SO_2)$

μ_{eff} 0.68 B.M.

2.5.20 SA.04 + Mn(II) + 2AP (**SAMn20**)

No reaction

2.5.21 SA.04 + Mn(II) + 3AP (**SAMn21**)

No reaction

2.5.22 SA.04 + Mn(II) + 4AP (**SAMn22**)

No reaction

3. Physical properties of Sulfonamides and Metal complexes

Physical properties and structure of sulfonamides and metal complexes are portrayed in the following Tables 4-5.

TABLE 4 PHYSICAL PROPERTIES AND PERCENTAGE YIELD OF SULFONAMIDES

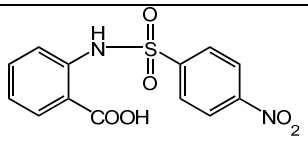
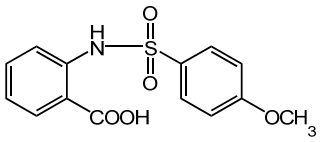
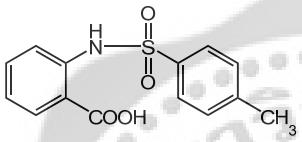
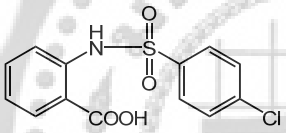
Compound	Structure	Physical property	Melting (^{o}C)	%Yield
SA.01		Pale white powder	209-212	96
SA.02		Pale white powder	171-173	98
SA.03		Pale white powder	186-189	96
SA.04		Pale white powder	177-180	80

TABLE 5 PHYSICAL PROPERTIES AND PERCENTAGE YIELD OF METAL COMPLEXES

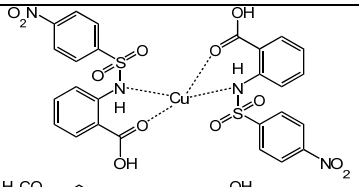
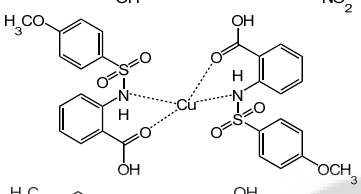
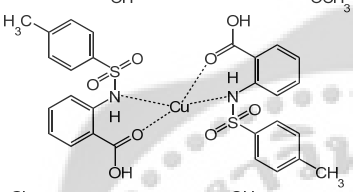
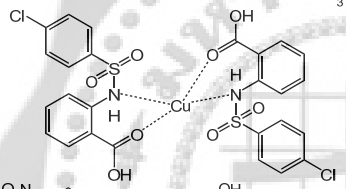
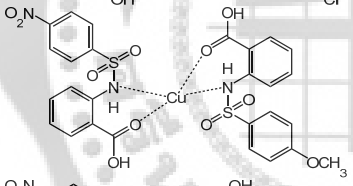
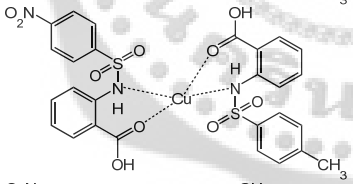
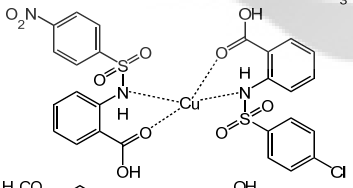
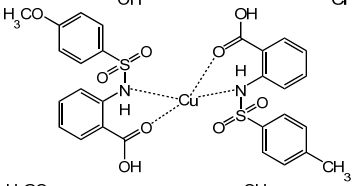
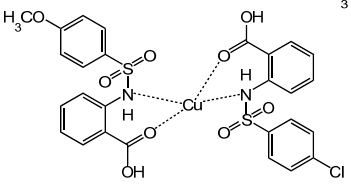
Compound	Structure	Physical property	Melting (^{o}C)	%Yield
SACu1		Blue-green powder	270-275	86
SACu2		Blue-green powder	265-272	57
SACu3		Blue-green powder	270-275	40
SACu4		Blue-green powder	270-275	43
SACu5		Blue-green powder	270-275	47
SACu6		Blue-green powder	270-275	40
SACu7		Blue-green powder	265-270	55
SACu8		Blue-green powder	272-276	5
SACu9		Blue-green powder	270-275	21

TABLE 5 (continued)

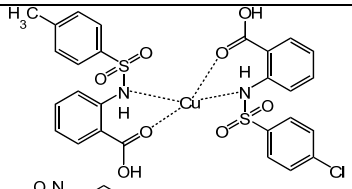
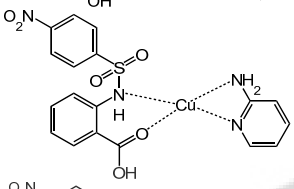
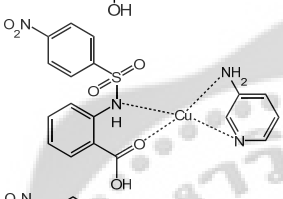
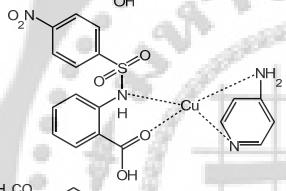
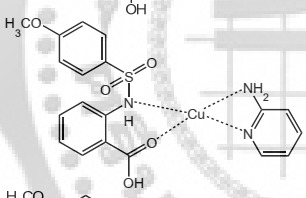
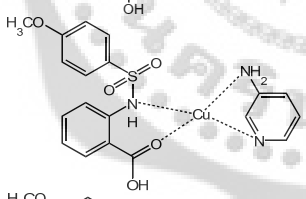
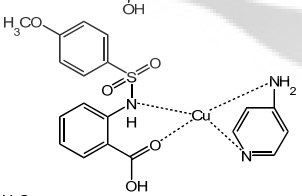
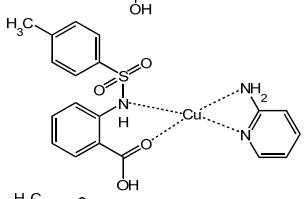
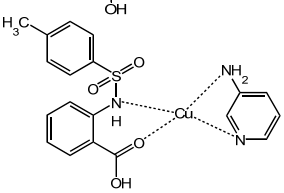
Compound	Structure	Physical property	Melting (°C)	%Yield
SACu10		Blue-green powder	270-282	14
SACu11		Blue-green powder	265-270	31
SACu12		Blue-green powder	260-265	57
SACu13		Blue-green powder	265-270	29
SACu14		Blue-green powder	275-280	62
SACu15		Blue-green powder	270-275	53
SACu16		Blue-green powder	270-273	60
SACu17		Blue-green powder	278-282	39
SACu18		Blue-green powder	260(d)	39

TABLE 5 (continued)

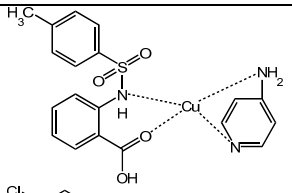
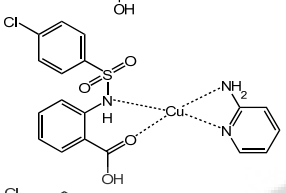
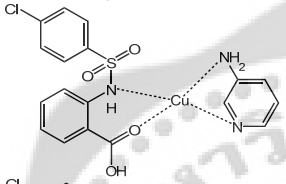
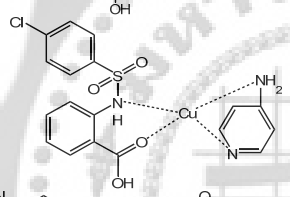
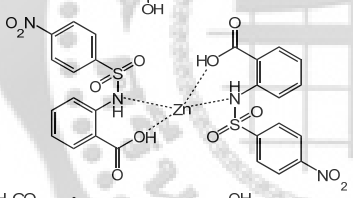
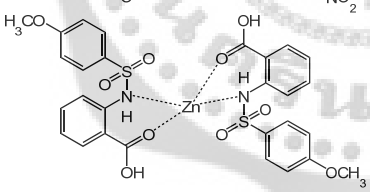
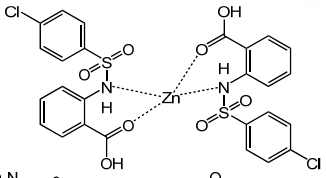
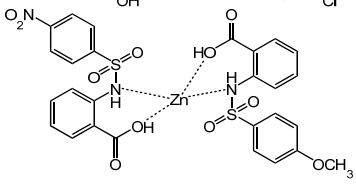
Compound	Structure	Physical property	Melting (°C)	%Yield
SACu19		Blue-green powder	280-286	59
SACu20		Blue-green powder	270-275	54
SACu21		Blue-green powder	270-275	52
SACu22		Blue-green powder	285-290	56
SAZn1		White solid	252-270	9
SAZn2		White solid	185-190	58
SAZn3	-	NR	NR	NR
SAZn4		White solid	195-200	1
SAZn5		Pale white solid	240-250	6

TABLE 5 (continued)

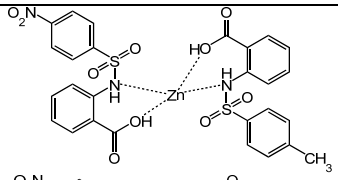
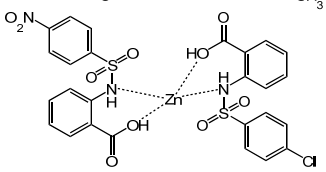
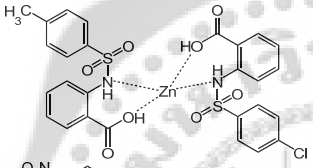
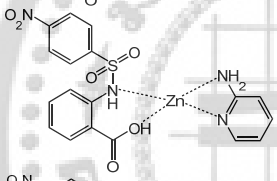
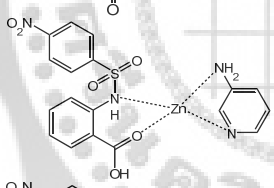
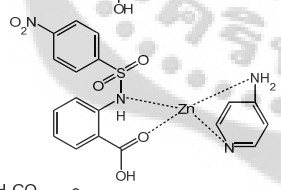
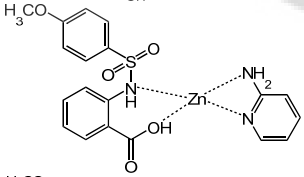
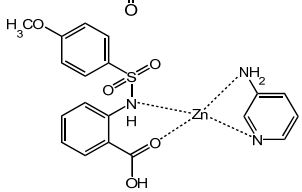
Compound	Structure	Physical property	Melting (^{o}C)	%Yield
SAZn6		Pale white solid	255-270	4
SAZn7		White solid	260-275(d)	4
SAZn8	-	NR	NR	NR
SAZn9	-	NR	NR	NR
SAZn10		White solid	235-248	5
SAZn11		Pale white solid	265-275	4
SAZn12		Burnt orange solid	280(d)	74
SAZn13		Pale yellow solid	285-290(d)	69
SAZn14		White solid	260-265	1
SAZn15		Raw umber solid	200-225(d)	60

TABLE 5 (continued)

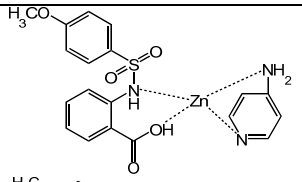
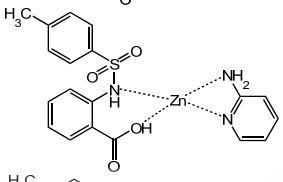
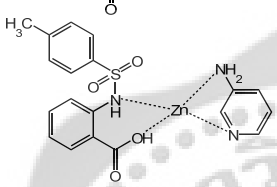
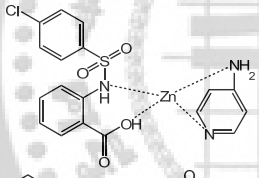
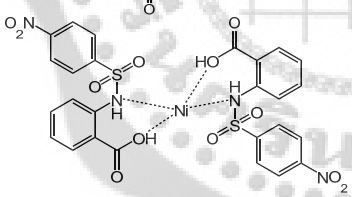
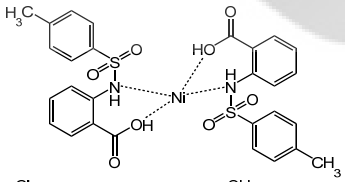
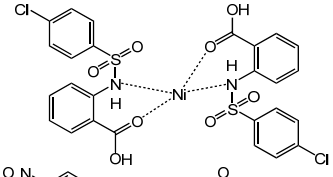
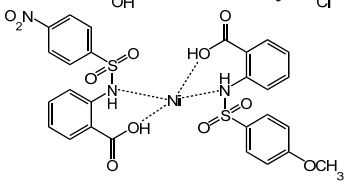
Compound	Structure	Physical property	Melting (°C)	%Yield
SAZn16		White solid	270-275	1
SAZn17		White solid	255-270	6
SAZn18		Raw umber solid	200-220	16
SAZn19	-	NR	NR	NR
SAZn20	-	NR	NR	NR
SAZn21	-	NR	NR	NR
SAZn22		White solid	235-240	5
SANi1		Pale white solid	255-270	8
SANi2	-	NR	NR	NR
SANi3		White solid	255-265	11
SANi4		Aquamarine solid	190-200	53
SANi5		White solid	255-290	8

TABLE 5 (continued)

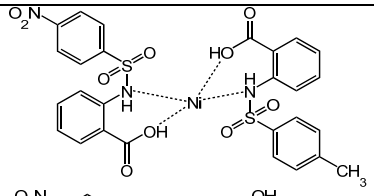
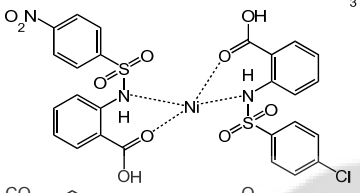
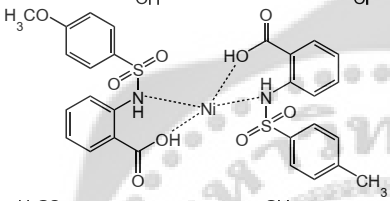
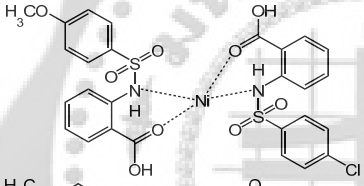
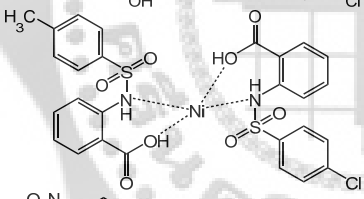
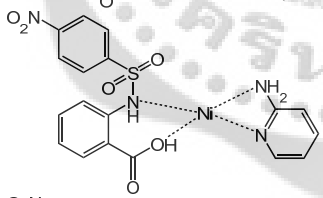
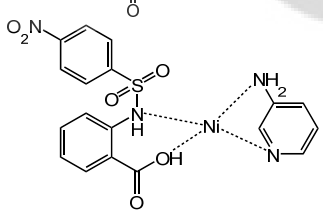
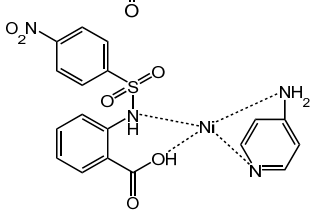
Compound	Structure	Physical property	Melting (°C)	%Yield
SANi6		White solid	230-235	9
SANi7		Blue-green solid	200-205	56
SANi8		White solid	235-240	9
SANi9		Blue-green solid	173-205	26
SANi10		White solid	225-250	5
SANi11		Pale white solid	260-265	8
SANi12		Fallow solid	265-268	8
SANi13		Pale white solid	265-268	46

TABLE 5 (continued)

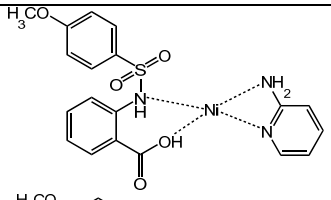
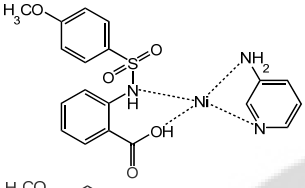
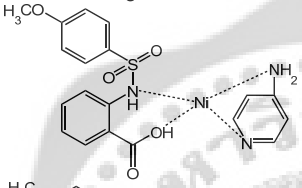
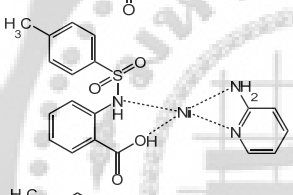
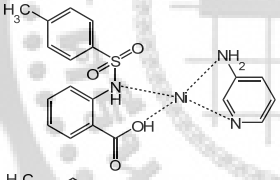
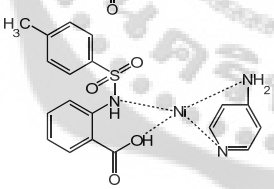
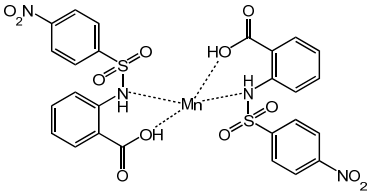
Compound	Structure	Physical property	Melting (°C)	%Yield
SANi14		White solid	265-275	2
SANi15		Pale white solid	270-275	1
SANi16		White solid	268-275	2
SANi17		White solid	260-275	7
SANi18		Fallow solid	260-275	6
SANi19		White solid	260-275	6
SANi20	-	NR	NR	NR
SANi21	-	NR	NR	NR
SANi22	-	NR	NR	NR
SAMn1		White solid	250-260	9
SAMn2	-	NR	NR	NR

TABLE 5 (continued)

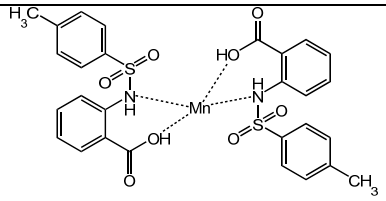
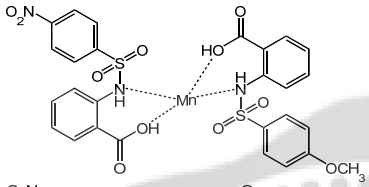
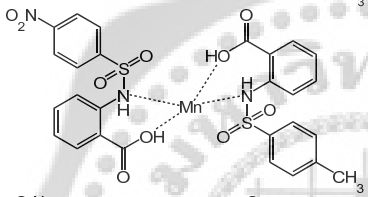
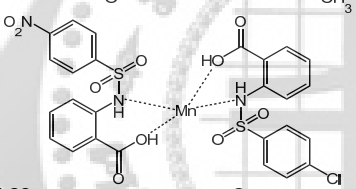
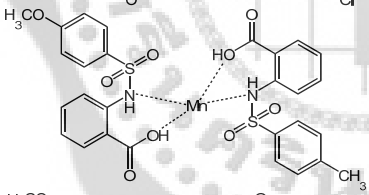
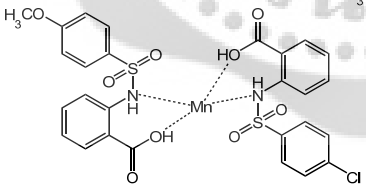
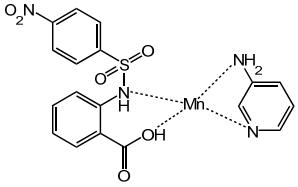
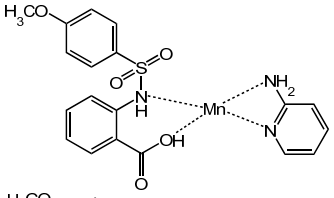
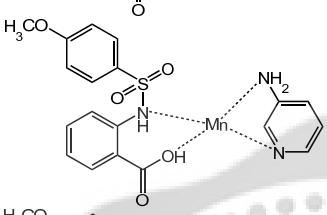
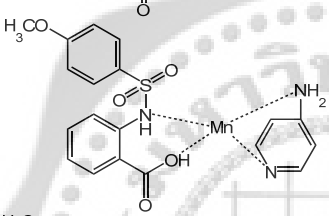
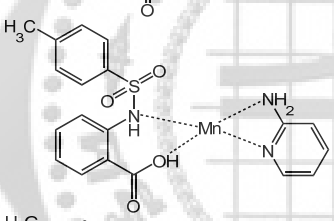
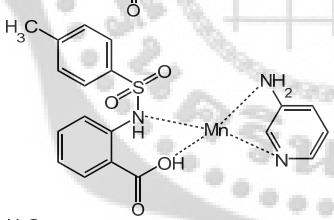
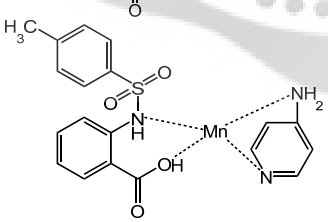
Compound	Structure	Physical property	Melting (^{o}C)	%Yield
SAMn3		White solid	235-265	12
SAMn4	-	NR	NR	NR
SAMn5		Pale white solid	255-260	7
SAMn6		Pale white solid	230-235	6
SAMn7		Pale white solid	255-260	7
SAMn8		White solid	235-240	1
SAMn9		White solid	240-260(d)	7
SAMn10	-	NR	NR	NR
SAMn11	-	NR	NR	NR
SAMn12		Pale white solid	258-265	4

TABLE 5 (continued)

Compound	Structure	Physical property	Melting (°C)	%Yield
SAMn13	-	NR	NR	NR
SAMn14		White solid	265-275	1
SAMn15		White solid	265-275	1
SAMn16		White solid	265-270	1
SAMn17		White solid	240-282	7
SAMn18		White solid	240-282	8
SAMn19		White solid	230-235	8
SAMn20	-	NR	NR	NR
SAMn21	-	NR	NR	NR
SAMn22	-	NR	NR	NR

Note : d = decomposed, NR = no reaction.

4. Infrared spectra

The IR spectra of metal complexes were analyzed by comparing with the free ligands; e.g. sulfonamides (**21**) and 2-, 3-, 4-aminopyridines. The sulfonamides are molecules with multifunctional groups e.g. sulfonamide, carboxyl and nitro that can form complexes with metal ions. Considering the IR spectra of the free ligands and their metal complexes (Table 6), it was found that the NH of SO_2NH and C=O, O-H of CO_2H involve in coordination with metal ions.

The sulfonamide **SA.01** showed absorption bands at 3449 and 1393 cm^{-1} of the stretching and bending vibration of O-H, respectively. The absorption bands of ν(N-H) showed one stretching band at 3196 cm^{-1} and two bending bands at 1582 and 758 cm^{-1} for δ(N-H). With regard to the characteristic vibration of the sulfamido group, the bands assigned to the $\nu(SO_2)$ appeared at 1318 and 1162 cm^{-1} and the ν(S-N) vibration showed at 926 cm^{-1}. The absorption of nitro group appeared at 1531 and 1349 cm^{-1}. The carboxyl group exhibited strong band at 1665 cm^{-1}. In addition to the main absorption bands, ν(C-O) and ν(C-N) displayed at 1086 and 1264 cm^{-1}, respectively. Similarly, other sulfonamides such as **SA.02**, **SA.03** and **SA.04** show the absorption bands as described for **SA.01**.

2-, 3-, 4-Aminopyridines are free ligands in this study. The IR spectra of 2-aminopyridine showed stretching bands ν(N-H) at 3449, 3312 cm^{-1} and bending bands δ(N-H) at 1560, 767 cm^{-1}. The C-N and C=N stretching modes of 2-aminopyridine are recorded at 1343, 1325 cm^{-1} and 1629 cm^{-1}, respectively. The IR spectra of 3-aminopyridine and 4-aminopyridine exhibit similar absortion pattern as 2-aminopyridine (Table 6).

The IR spectra of the metal complexes were determined by comparing the presence or absence or the shift of stretching or bending frequencies with their ligands. The result show that all Cu complexes of sulfonamides and sulfonamides with 2-, 3-, 4-aminopyridines (**SACu1**-**SACu22**) from through NH of $NHSO_2$ and C=O of CO_2H moieties. As seen from the IR spectra, aminopydines use N atom of pyridine ring and NH_2 substituted group at C-2, C-3 and C-4 positions.

Similar coordinations were noted for Zn-complexes (**SAZn4**, **12**, **13**, **15**) and Ni-complexes (**SANi4**, **7**, **9**). Some of the sulfonamide metal complexes resulted from OH (of CO_2H) coordinationating, instead of CO (of CO_2H), with metal ions as indicated by the strong C=O absorption at 1698-1718 cm^{-1} such as Ni-complexes (**SANi1**, **3**, **5**, **6**, **8**, **10**-**19**) and all of the synthesized Mn-complex (**SAMn1**-**9**, **12**, **14**, **19**).

5. Magnetic properties

Magnetic susceptibility of the metal complexes were performed at room temperature. The tested metal complexes possess paramagnetic property with magnetic moment (μ_{eff}) of 0.67 - 0.93 B.M. (Table 6).

TABLE 6 FT-IR SPECTROSCOPIC AND MAGNETIC MOMENT (μ_{eff}) DATA OF FREE LIGANDS AND METAL COMPLEXES

Comp.	IR Spectra, cm^{-1}											μ_{eff}
	ν(C=O)	ν(C–O)	ν(C–N)	ν(O–H)	δ(O–H)	ν(N–H)	δ(N–H)	$\nu(SO_2)$	ν(S–N)	ν(C=N)	$\nu(NO_2)$	(BM.)
SA.01	1665(s)	1086(s)	1264(s)	3449(m, br)	1393(m, sh)	3196(m, sh)	1582(m), 758(s)	1318(m), 1162(vs)	926(s)	-	1531(vs), 1349(s)	-
SA.02	1678(s)	1092(s), 1022(s)	1261(s)	3492(m, br)	1389(s)	3202(s, sh)	1581(s), 754(s)	1344(m), 1160(s)	926(s)	-	-	-
SA.03	1675(s)	1089(s)	1258(s)	3449(w, br)	1389(m)	3201(m, sh)	1585(m), 754(s)	1342(s), 1162(s)	922(s)	-	-	-
SA.04	1662(s)	1093(s)	1261(m)	3442(w, br)	1380(s)	3188(w, sh)	1585(s), 753(s)	1342(s), 1164(s)	929(s)	-	-	-
2AP	-	-	1343(m), 1325(m)	-	-	3449(m, sh), 3312(w, br)	1560(s), 767(s)	-	-	1629(s)	-	-
3AP	-	-	1294(s), 1262(s)	-	-	3377(s, br), 3203(w, br)	1588(s), 708(s)	-	-	1634(s)	-	-
4AP	-	-	1334(s), 1270(s)	-	-	3439(s), 3304(s)	1562(s), 823(s)	-	-	1652(s)	-	-
SACu1	-	1091(m, sh)	1276(s)	3475(m, br)	1394(s, sh)	-	-	1314(m), 1164(vs)	945(s)	-	1531(s), 1394(vs)	0.82
SACu2	-	1096(s), 1025(m)	1264(s)	3471(m, br)	1397(s)	-	-	1330(m, br), 1153(s)	931(s, br)	-	-	0.79
SACu3	-	1090(s)	1268(s)	3554(s, sh), 3493(m, sh)	1394(vs)	-	-	1331(m), 1169(s)	927(s)	-	-	0.93
SACu4	-	1095(s)	1279(s)	3465(m, br)	1396(vs)	-	-	1335(m), 1159(s)	937(s, br)	-	-	0.69

TABLE 6 (continued)

Comp.	IR Spectra, cm^{-1}											μ_{eff}
	ν(C=O)	ν(C–O)	ν(C–N)	ν(O–H)	δ(O–H)	ν(N–H)	δ(N–H)	$\nu(SO_2)$	ν(S–N)	ν(C=N)	$\nu(NO_2)$	(BM.)
SACu5	-	1093(s), 1024(w)	1274(s)	3448(s, br)	1396(vs)	-	-	1161(s)	938(s, br)	-	1534(s), 1350(s)	0.80
SACu6	-	1091(s)	1274(m)	3449(s, br)	1396(vs)	-	-	1163(vs)	941(m, br)	-	1534(s), 1350(s)	0.80
SACu7	-	1093(s)	1274(s)	3450(s, br)	1396(vs)	-	-	1161(vs)	941(m, br)	-	1534(s), 1350(s)	0.84
SACu8	-	1093(m), 1024(vw)	1267(m)	3449(s, br)	1396(s)	-	-	1156(s)	934(w, br)	-	-	0.54
SACu9	-	1093(s), 1024(w)	1274(s)	3449(m, br)	1396(vs)	-	-	1332(w), 1156(vs)	938(m, br)	-	-	0.82
SACu10	-	1094(s)	1275(s)	3448(s, br)	1396(vs)	3181(w, br)	-	1334(m), 1158(vs)	936(s, br)	-	-	0.82
SACu11	-	1090(m)	1276(m)	3460(s, br)	1394(s)	3101(w, sh)	773(s)	1317(s), 1164(s)	943(s, br)	-	1537(s), 1349(s)	0.69
SACu12	-	1090(s)	1276(s)	3474(s, br)	1394(s)	3101(w, sh)	773(s)	1314(w), 1164(s)	944(s, br)	-	1538(s), 1349(s)	0.69
SACu13	-	1091(s)	1276(s)	3474(s, br)	1394(vs)	3100(m, sh)	773(s)	1314(m), 1165(vs)	945(s, br)	-	1531(s), 1349(s)	0.69
SACu14	-	1095(s), 1024(s)	1264(s)	3449(s, br)	1396(vs)	3181(m, br)	1560(s), 767(s)	1332(m), 1154(vs)	934(s, br)	-	-	0.68
SACu15	-	1093(s), 1024(s)	1263(s)	3449(m, br)	1396(s, sh)	3188(m, br)	764(s)	1154(vs)	934(m, br)	-	-	0.68

TABLE 6 (continued)

Comp.	IR Spectra, cm^{-1}											μ_{eff}
	ν(C=O)	ν(C–O)	ν(C–N)	ν(O–H)	δ(O–H)	ν(N–H)	δ(N–H)	$\nu(SO_2)$	ν(S–N)	ν(C=N)	$\nu(NO_2)$	(BM.)
SACu16	-	1095(s), 1024(s)	1264(s)	3448(s, br)	1396(vs)	3196(m, br)	768(s)	1153(vs)	932(s, br)	-	-	0.68
SACu17	-	1089(s)	1268(s)	3555(s, br)	1394(vs)	3492(s, br)	768(s)	1170(vs)	927(s)	-	-	0.68
SACu18	-	1089(s)	1267(s)	3555(s, br)	1394(vs)	3130(m, br)	768(s, sh)	1170(vs)	927(s, sh)	-	-	0.68
SACu19	-	1090(s, sh)	1268(s, sh)	3555(s, br)	1394(vs)	3492(s ,br)	1598(s)	1170(vs)	927(s, sh)	-	-	0.68
SACu20	-	1095(vs)	1280(s)	3464(s, br)	1396(vs)	3174(m, br)	754(s)	1159(vs)	938(s, br)	-	-	0.72
SACu21	-	1095(vs)	1280(s)	3473(s, br)	1396(vs)	3181(m, br)	754(s)	1159(vs)	939(s, br)	-	-	0.72
SACu22	-	1095(s, sh)	1280(s, sh)	3464(s, br)	1396(vs)	3156(m, br)	754(s)	1159(vs)	938(s)	-	-	0.72
SAZn1	1709(vs)	1082(s)	1249(m)	3449(m, br)	1382(s)	-	-	1306(m), 1183(vs)	961(m)	-	1534(vs), 1352(s)	0.82
SAZn2	-	1095(s), 1025(s)	1265(s)	3449(m, br)	1397(s)	-	-	1326(m), 1153(vs)	935(s)	-	-	0.79
SAZn3	-	-	-	-	-	-	-	-	-	-	-	-
SAZn4	-	1095(s)	1279(m)	3449(w, br)	1396(s)	-	-	1158(s)	941(m, br)	-	-	0.86
SAZn5	1717(s)	1082(s)	1249(m)	3446(m, br)	1376(m)	-	-	1305(m), 1183(s)	963(s)	-	1541(vs), 1351(s)	0.81
SAZn6	1708(s)	1082(s)	1249(m)	3450(s, br)	1374(m)	-	-	1306(m), 1183(vs)	963(s)	-	1541(vs), 1351(s)	0.81
SAZn7	1709(vs)	1082(s)	1249(s)	3446(m, br)	1382(s)	-	-	1306(s), 1183(vs)	960(s)	-	1540(vs), 1352(s)	0.84
SAZn8	-	-	-	-	-	-	-	-	-	-	-	-
SAZn9	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 6 (continued)

Comp.	IR Spectra, cm^{-1}											μ_{eff}
	ν(C=O)	ν(C–O)	ν(C–N)	ν(O–H)	δ(O–H)	ν(N–H)	δ(N–H)	$\nu(SO_2)$	ν(S–N)	ν(C=N)	$\nu(NO_2)$	(BM.)
SAZn10	1702(s)	1080(s)	1249(s)	3446(m, br)	1375(s)	-	-	1175(vs)	960(m)	-	-	1.08
SAZn11	1718(s)	1084(m)	1274(m, br)	3447(w, br)	1373(m)	-	-	1306(m, br), 1183(s)	961(w, br)	-	1542(vs), 1373(m)	0.69
SAZn12	-	1087(s)	1273(s)	3463(s, br)	1410(s)	3372(s, br)	1577(m), 737(s)	1145(vs)	972(s)	-	1524(vs), 1352(s)	0.69
SAZn13	-	1087(s)	1262(m), 1281(m, br)	3463(s, br)	1404(s, br)	3363(s, br)	1576(m), 738(s, br)	1147(s, sh)	968(s)	-	1526(vs), 1352(s)	0.69
SAZn14	1699(s, sh)	1082(s), 1018(s)	1263(s)	3442(w, br)	1374(s)	-	1560(s, sh), 777(m)	1164(s)	955(m)	-	-	0.89
SAZn15	-	1094(s), 1026(m)	1267(s)	3466(m, br)	1389(s)	3376(s, br)	1597(s), 763(s)	1155(vs)	940(m, br)	-	-	0.75
SAZn16	1699(s)	1080(s), 1020(s)	1265(s)	3442(s, br)	1374(s)	-	830(s)	1164(vs)	960(m)	-	-	0.68
SAZn17	1718(s)	1081(m)	1252(m)	3444(w, br)	1396(s)	-	1560(s), 718(m)	1174(s)	959(m, br)	-	-	0.68
SAZn18	1702(s)	1080(s)	1249(m)	3444(m, br)	1376(s)	-	1560(s, sh)	1174(s)	960(m, br)	1638(m, sh)	-	0.68
SAZn19	-	-	-	-	-	-	-	-	-	-	-	-
SAZn20	-	-	-	-	-	-	-	-	-	-	-	-
SAZn21	-	-	-	-	-	-	-	-	-	-	-	-
SAZn22	1705(s)	1080(s)	1306(s), 1249(s)	3442(m, br)	1374(s)	-	1560(m, sh)	1174(s)	960(s, br)	1654(m, sh)	-	0.72
SANi1	1709(vs)	1092(s)	1249(m)	3448(m, br)	1374(m, sh)	-	-	1306(s), 1183(vs)	958(m)	-	1540(vs), 1351(s)	0.82

TABLE 6 (continued)

Comp.	IR Spectra, cm^{-1}											μ_{eff}
	ν(C=O)	ν(C–O)	ν(C–N)	ν(O–H)	δ(O–H)	ν(N–H)	δ(N–H)	$\nu(SO_2)$	ν(S–N)	ν(C=N)	$\nu(NO_2)$	(BM.)
SANi2	-	-	-	-	-	-	-	-	-	-	-	-
SANi3	1702(vs)	1083(s)	1248(s)	3450(w, br)	1375(m)	-	-	1175(s)	959(m)	-	-	0.79
SANi4	-	1095(s)	1276(m)	3450(w, br)	1396(s)	-	-	1339(m), 1157(s)	947(m)	-	-	0.90
SANi5	1717(s)	1081(s)	1249(s)	3446(m, br)	1375(s)	-	-	1306(s), 1181(s)	959(m)	-	1542(vs), 1376(s)	0.80
SANi6	1717(s)	1081(s)	1249(s)	3446(m, br)	1375(s)	-	-	1306(s), 1181(s)	959(m)	-	1542(vs), 1376(s)	0.80
SANi7	-	1094(s, sh)	1274(s)	3447(s, br)	1388(s, br)	-	-	1319(m, br), 1158(vs)	950(s, br)	-	1540(s, sh), 1351(m)	0.93
SANi8	1702(s)	1079(s)	1247(m)	3445(m, br)	1375(s)	-	-	1174(s)	959(w)	-	-	0.79
SANi9	-	1095(s)	1269(m)	3446(m, br)	1396(s)	-	-	1340(m, sh), 1154(s)	949(w, br)	-	-	1.16
SANi10	1702(s)	1080(s)	1246(m)	3447(m, br)	1374(s)	-	-	1175(s)	963(m)	-	-	0.82
SANi11	1717(s)	1082(s)	1249(m)	3449(m, br)	1374(s, br)	-	1560(m, sh), 742(s, sh)	1183(vs)	960(m, br)	-	1541(vs)	0.69
SANi12	1716(s)	1082(s)	1249(m)	3442(m, br)	1374(s)	3113(s br)	-	1183(vs)	960(s)	-	1540(vs), 1352(s)	0.69
SANi13	1709(s, sh)	1083(s)	1249(m)	3442(w, br)	1394(vs)	3100(m, sh)	773(s)	1314(m), 1165(vs)	945(s, br)	-	1531(s), 1349(s)	0.69
SANi14	1701(vs)	1080(s), 1019(s)	1264(s)	3448(m, br)	1374(m, sh)	-	1596(vs), 775(w, sh)	1164(vs)	960(s)	-	-	0.68

TABLE 6 (continued)

Comp.	IR Spectra, cm^{-1}											μ_{eff}
	ν(C=O)	ν(C–O)	ν(C–N)	ν(O–H)	δ(O–H)	ν(N–H)	δ(N–H)	$\nu(SO_2)$	ν(S–N)	ν(C=N)	$\nu(NO_2)$	(BM.)
SANi15	1702(s)	1082(s), 1019(s)	1263(s)	3446(s, br)	1374(s)	-	1596(s), 776(m)	1164(vs)	949(m)	-	-	0.68
SANi16	1699(vs)	1081(s), 1019(s)	1263(s)	3448(s, br)	1373(s)	-	831(s)	1164(vs)	960(s)	-	-	0.68
SANi17	1703(vs)	1080(s)	1249(s)	3449(m, br)	1375(s)	-	723(s)	1174(vs)	-	-	-	0.68
SANi18	1702(s)	1080(s)	1248(s)	3428(m, br)	1375(s)	-	722(m)	1174(s)	959(m, br)	-	-	0.82
SANi19	1702(s)	1080(s)	1250(m), 1306(s)	3447(m, br)	1376(s)	-	723(s)	1174(vs)	961(m, br)	-	-	0.79
SANi20	-	-	-	-	-	-	-	-	-	-	-	-
SANi21	-	-	-	-	-	-	-	-	-	-	-	-
SANi22	-	-	-	-	-	-	-	-	-	-	-	-
SAMn1	1708(vs)	1082(m, sh)	1248(m)	3448(m, br)	1374(m, sh)	-	-	1306 (s), 1183 (vs)	960 (m)	-	1541 (vs), 1353 (s)	0.82
SAMn2	-	-	-	-	-	-	-	-	-	-	-	-
SAMn3	1702(vs)	1080(s)	1249(s)	3448 (w, br)	1375(s)	-	-	1305(s), 1174(vs)	960(m)	-	-	0.79
SAMn4	-	-	-	-	-	-	-	-	-	-	-	-
SAMn5	1707(s)	1082(s)	1250(s)	3448(s, br)	1374(s)	-	-	1306(s), 1181(vs)	958(s)	-	1541(vs), 1353(m)	0.80
SAMn6	1707(s)	1082(s)	1250(s)	3448(s, br)	1374(s)	-	-	1306(s), 1181(vs)	958(s)	-	1541(vs), 1353(m)	0.73

TABLE 6 (continued)

Comp.	IR Spectra, cm^{-1}											μ_{eff}
	ν(C=O)	ν(C–O)	ν(C–N)	ν(O–H)	δ(O–H)	ν(N–H)	δ(N–H)	$\nu(SO_2)$	ν(S–N)	ν(C=N)	$\nu(NO_2)$	(BM.)
SAMn7	1817(s)	1081(s)	1256(m)	3449(m, br)	1375(s)	-	-	1307(m), 1183(vs)	960(w, br)	-	1541(vs), 1352(s)	0.84
SAMn8	1702(s)	1082(m)	1246(m)	3445(w, br)	1375(s)	-	-	1175(s)	959(w)	-	-	0.79
SAMn9	1699(s)	1082(s), 1018(m)	1265(s)	3446(m, br)	1374(s)	-	-	1164(s)	959(w)	-	-	0.82
SAMn10	-	-	-	-	-	-	-	-	-	-	-	-
SAMn11	-	-	-	-	-	-	-	-	-	-	-	-
SAMn12	1716(s)	1082(s)	1249(s)	3446(m, br)	1374(m, sh)	-	742(s)	1183(vs)	960(m, br)	-	1540(vs), 1351(m, br)	0.69
SAMn13	-	-	-	-	-	-	-	-	-	-	-	-
SAMn14	1698(vs)	1082(s), 1016(s)	1263(s)	3447(w, br)	1374(s)	-	1560(s), 755(w, s)	1164(s)	949(m)	-	-	0.68
SAMn15	1699(s, sh)	1080(m), 1020(w)	1263(m)	-	1397(m, sh)	-	-	1162(m)	-	-	-	0.68
SAMn16	1699(s)	1081(s), 1020(s)	1262(s)	3448(w, br)	1374(s)	-	1559(s), 833(s)	1164(s)	957(m)	1654(s)	-	0.68
SAMn17	1718(s)	1081(m)	1252(m)	3448(w, br)	1396(s)	-	1560(s), 718(m)	1174(s)	959(m, br)	-	-	0.68
SAMn18	1702(s)	1080(s)	1249(m)	3444(m, br)	1376(s)	-	1560(s, sh), 723(s)	1175(vs)	960(m, br)	-	-	0.68
SAMn19	1702(s)	1080(s)	1250(m),	3449(m, br)	1375(m, br)	-	1560(m, sh), 723(s)	1174(vs)	961(m, sh)	1654(s, sh)	-	0.68
SAMn20	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 6 (continued)

Comp.	IR Spectra, cm^{-1}											μ_{eff}
	ν(C=O)	ν(C–O)	ν(C–N)	ν(O–H)	δ(O–H)	ν(N–H)	δ(N–H)	$\nu(SO_2)$	ν(S–N)	ν(C=N)	$\nu(NO_2)$	(BM.)
SAMn21	-	-	-	-	-	-	-	-	-	-	-	-
SAMn22	-	-	-	-	-	-	-	-	-	-	-	-

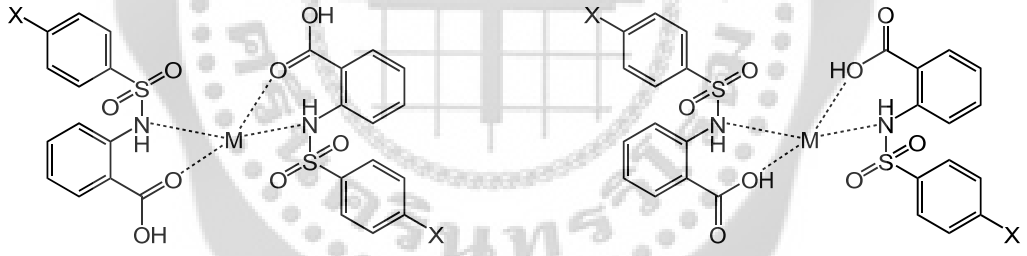
Note: vs = Very strong, s = strong, m = medium, vw = very weak, w = weak, br = broad, sh = shape

CHAPTER 5

CONCLUSION

Sulfomamide derivatives have been synthesized by the reaction of anthranilic acid and arenesulfonyl chlorides in 80-98 %yield. The metal complexes were achieved from 1 : 1 : 1 mol ratio of the sulfonamides (**21** denoted as **L1**) with the sulfonamides and/or difference ligands; 2-, 3-, 4-aminopyridine (**L2**) and metal salts (**$MY_2 \cdot nH_2O$**) to provide **L1-M-L2** metal complexes. The structure of these sulfonamides and their metal(II) complexes have been determined by FT-IR spectra and magnetic moment data.

In this study, the coordination of sulfonamides (**21**) were formed using of one O donor atom from carboxyl or hydroxyl group (CO_2H) and N donor atom of the sulfamido ($NHSO_2$) for chelating to afford the metal complexes (**72** and **73**). Similarly, the sulfonamides (**21**) coordinated with aminopyridines (using N atom donor of NH_2 and ring N) to give metal complexes **74-75** as shown in Figure 29.

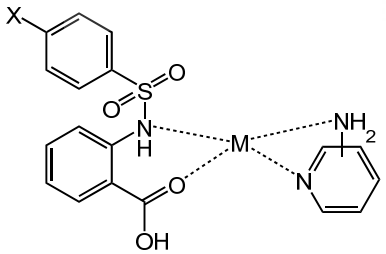


(**72**)

M = Cu, Zn, Ni

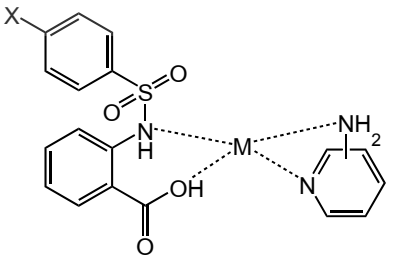
(**73**)

M= Zn, Ni, Mn



(**74**)

M = Cu, Zn, Ni



(**75**)

M = Zn, Ni, Mn

X = NO_2, OCH_3, CH_3, Cl

Figure 29 Structure of coordination compounds (**72-75**)

Suggestions and Comments

The sulfonamides metal complexes were synthesized as powder. Attempts have been made to recrystallize the compounds for single crystal X-ray crystallography. Bioactivity testings of the synthesized compounds are being under investigated.

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GLOSSARY

LIST OF ABBREVIATIONS AND SYMBOLS

ADR	Antidrug resistance
Ac	Acetyl group
AcOH	Acetic acid
Bn	Benzyl group
dppf	1,1'-*bis*(diphenylphosphanyl)ferrocene
br	Broad (for IR and NMR data)
δ	Bending vibration (for IR data) and Chemical shift (for NMR data)
$CHCl_3$	Chloroform
J	Coupling constant
COX-2	Cyclooxygenase-2
cm^{-1}	Reciprocal centimeter (unit of wave number)
DMSO-d_6	Deuterated dimethyl sulfoxide
DCM	Dichloromethane
Et_2O	Diethyl ether
DMF	Dimethylformamide
d	Doublet (for NMR data)
dd	Doublet of doublets (for NMR data)
EtOH	Ethanol
EDC	Ethylene dichloride
EtOAc	Ethyl acetate
Et	Ethyl
g	Gram
GI_{50}	50% Growth inhibition
CIC_{50}	Growth to 50% of the control cell viability
Hz	Hertz
h	Hour
IR	Infrared
IC_{50}	50% Inhibitory Concentration
μ_{eff}	Magnetic moment
m	Medium (for IR data)
Me	Methyl

LIST OF ABBREVIATIONS AND SYMBOLS (continued)

MeOH	Methanol
μM	Micro molar
mg	Milligram
mL	Milliliter
mmol	Milli molar
MIC	Minimum Inhibitory Concentration
MIC_{50}	Minimum Inhibitory Concentration of 50% of isolates
nM	nano molar
NMR	Nuclear Magnetic Resonance
p-TosOH	*para*-toluenesulfonic acid
Ph	Phenyl
KBr	Potassium bromide
t-BuOK	Potassium tertiary butoxide
Py	Pyridine
Rt	Room temperature
sh	Shape (for IR data)
s	Singlet (for NMR data) and Strong (for IR data)
SOD	Super oxide dismutase
ν	Stretching vibration (for IR data)
TBS	Tertiary-butyl dimethyl silyl
THF	Tetrahydrofuran
Et_3N	Triethylamine
Tf_2O	Trifluoromethanesulfonic acid
TMS-Cl	Trimethylsilyl chloride
PPh_3	Triphenylphosphine
t	Triplet (for NMR data)
TsCl	Tosyl chloride
vw	Very weak (for IR data)
v	Very strong (for IR data)
ν_{MAX}	Wave number at maximal absorption
W	Weak (for IR data)

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