IOSR Journal of Engineering (IOSRJEN)
e-ISSN: 2250-3021, **p**-ISSN: 2278-8719
Vol. 3, Issue 8 (August. 2013), ||V5|| PP 38-50

Synthesis And Characterization Of Co(Ii), Cu(Ii), Cd(Ii), Zn(Ii) And Ni(Ii) Complexes Of Schiff Base Ligand Derived From *S*-Benzyldithiocarbazate (Sbdtc) And Acetophenone With Their Biological Activity Studies.

Nadiah Ameram[a], Uwaisulqarni Othman[b]
[a]*Faculty of Earth Science, Universiti Malaysia Kelantan, 17600 Jeli*
[b]*Department of Chemistry, Faculty of Science and Technoogy, Universiti Malaysia Terengganu, Kuala Terengganu, 21030, Terengganu.*

Abstract: - A new Schiff Base ligand [(SBDTC)$_2$AP] has been synthesized by the 1:2 condensation of Acetophenone and *S*-benzyldithiocarbazate. A group of selected ions such as Cu(II), Cd(II), Zn(II), Ni(II) and Co(II) complexes of [(SBDTC)$_2$AP] have been prepared and characterized by elemental analysis, spectroscopic studies and various physico-chemical techniques included melting point determination, IR spectra and Uv-Vis spectra. Melting point of Schiff base is basically lower than metal complexes because of intra-molecular interaction. The FTIR spectrum for Schiff base ligand shows stretching vibration of the important functional group ;v(N-H) in range ~3179 cm^{-1},v(C=S) in range ~1103cm^{-1},v(N-N-C) in range ~1344cm^{-1},v(C=N) in range ~ 1599 cm^{-1} and lastly v(C-S-S) in range of 1027 cm^{-1}.As for the metal complexes of Schiff base, they posses in thiol form in solid state because of the v(N-H) and v(C=S) stretching disappearance near 3179 cm^{-1} and 1103 cm^{-1} respectively. The coordination of the azomethine nitrogen and sulfur donors atom to the metal is indicate by the shift on the v(C=N) band at 1599 cm^{-1} and in the v(C-S-S) band at 921 cm^{-1} .Finally the complexes have been evaluated for their biological activities against the selected bacteria. The Schiff Base exhibits moderate activities against *Staphylococcus aurieus, S.Typhy M.H.* and *Aeromonas sp*. All metal complexes were inactive against *S.Typhy M.H.*

Keywords: *- Synthesize, Characterize, Shift Base, Biologycal studies*

INTRODUCTION

Dithiocarbazic acid (Figure 1.0) and its derivatives have received considerable attention over the past few years (M. Akbar Ali *et al.*, 2000).One of the most fascinating example is SBDTC which is *S*-benzyldithiocarbazate (Figure 1.1) because it captivated researchers in this field to keep studying of this compound.

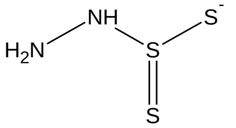


Figure 1.0 :dithiocarbazic acid

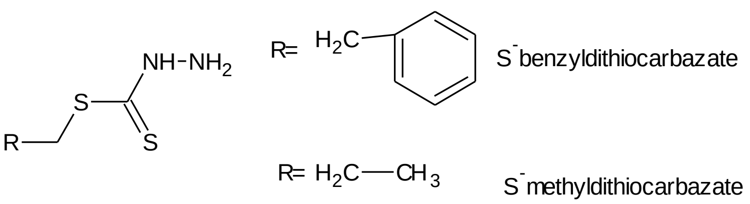


Figure 1.1: General structure for dithiocarbazate

SMDTC is an additional example which is *S*-methyldithiocarbazate. Both of them are isoelectronic to each other means that they have the same electronic configuration. It also has sulphur nitrogen chelating reagent. Mechanism tongue, S atom indithiocarbazate will act as a nucleophile which will then attack one of the carbon atom in benzyl chloride. Nucleophilic substitution reaction will occur initial of the reaction. Dithiocarbazic acid and the Schiff bases derived from its S-alkyl esters form an interesting series of ligands, whose properties can be greatly modified by introducing organic substituents into the ligand molecule by this means it inducing different stereochemistry in the resultant metal complexes. Undeniably, carcinostatic activities have already been found for some metal complexes of dithiocarbazic acid and the schiff bases derived from its *S*-methyl ester (Tarafdar *et al.*, 1976). More over they in this class of compounds, and their transition metal complexes they are potentially coordinate to dithiocarbazate in several ways to metals, depending on the nature of atom and also its substituents (Bonapasta *et al.*, 1980). Acetophenone (Figure 1.2) is the organic compound with the the chemical formula is C_8H_8O, and its molecular weight is 120.15 g/mol.

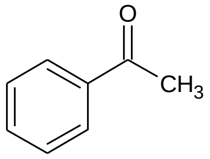


Figure 1.2:Acetophenone (AP)

Acetophenone occurs as a colourless liquid. It is slightly soluble in water. $C_6H_5C(O)CH_3$ is the simplest aromatic ketone. This chemical may be obtained by the dry distillation of mixture of the calcium salts of acetic and benzoic acids. Currently acetophenone mainly comes as a by-product of the phenol-acetone synthesis in the cumene oxidation process. At one time it was used as a hypnotic under the name of “hypnone”(M. Sittig., 1985). Reported in 2007 by Rao S.N. *et.al* has successfully synthesizing hap-SBDTC and hap-SMDTC Schiff bases derived from *o*-hydroxyacetophenone(hap) and *S*-benzyldithiocarbazate or *S*-methyldithiocarbazate, respectively. Both are dissymmetric tridentate ONS-donor schiff base ligands. Subsequently, it is useful in oxidation process in catalytic air oxidation of olefins with molybdenum dioxo complexes.

In this existing research, *S*-benzyldithiocarbazate (SBDTC)(Figure 1.1) will be use to form Schiff base ligand with acetophenone (Figure 1.2). What’s more, this reaction will continue with synthesizing metal complexes using acetate transition metals salts.

Schiff base are naturally formed by the condensation reaction of a primary amine and an aldehyde (Smith., 2006). The consequential functional group, $R_1HC=N-R_2$,(Figure 1.3(a)) is called an imine. Ketones, however will form imines of the type $R_1R_2C=N-R_3$.(Figure 1.3(b)).As well as acetophenone is a ketone, so the reactions tend to occur less readily than with aldehydes.

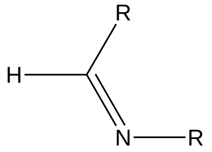


Figure1.3(a)

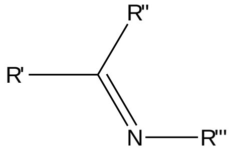
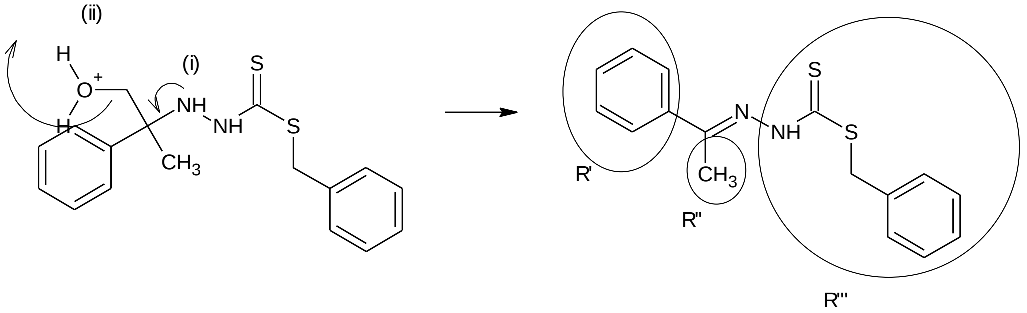


Figure1.3(b)

Tridentate ligand are less common than didentate and tetradentate ligand. However, they are useful for binding metal ions that can form stable 5-coordinate complexes with sufficiently bulky partner ligands or indeed the Schiff base itself, such as Cu(II) or Fe(II). The mechanism of schiff base formation can be divided into two clear-cut parts. Firstly is nucleophilic addition of the primary amine and secondly elimination of H_2O.(Figure 1.4).Basically, small molecule is eliminated during a reaction and in this case, water molecule, H_2O(Smith., 2006).



(i) Nucleophilic addition of the primary amine imines formation (ii) Elimination of H_2O

Figure 1.4 Mechanism of imine’s formation

In 2005, Mohamed *et al*. reported that each step involves a reversible equilibrium so that the reaction is driven to completion by removing H_2O. Based on that rationale, schiff base formation involves reaction called condensation reaction. In this research paper, schiff base ligand is formed from the reaction between *S*-

benzyldithiocarbazate and acetophenone. (Figure 1.5). Figure 1.6 below shows General structure of new dithiocarbazate Schiff base derived from acetophenone.

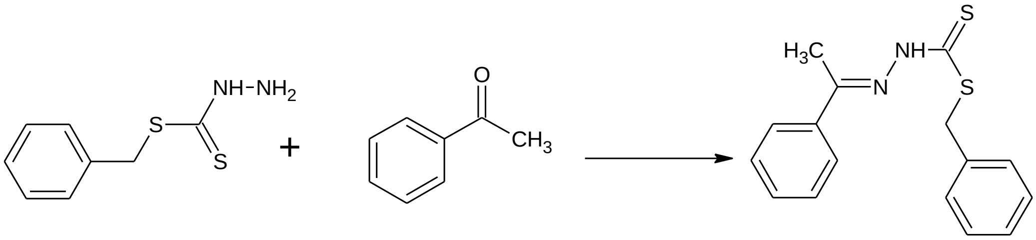


Figure 1.5: SBDTC+Acetophenone→benzyl(2*E*)-2-(phenylmethylidene)hydrazinecarbodithioate+ H_2O

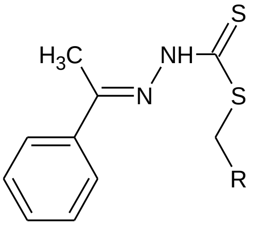


Figure 1.6 General structure of new dithiocarbazate Schiff base derived from acetophenone

2. Experimental

An electrothermal manual melting point instruments is use to determine the melting points of the compounds. All samples are place in glass tube and record the melting point of each sample after it starts to melt. Analyses of carbon, hydrogen, nitrogen and sulphur in the compounds are done by using FLASH EA 1112 series CHNS Analyzer at chemistry science department, University Malaysia Terengganu. The CHNS analyzer was already calibrated by laboratory assistant.

Infrared spectra of the samples are recorded as KBr pellets on an FT-IR spectrometer (Perkin-Elmer) spectrum 100 at the Chemistry Science Department, Universiti Malaysia Terengganu. All the spectra are run in the range 400-4000cm-1 at room temperature. The UV-Vis spectra are record by using quartz cuvettes in the region of 200-800 nm. Type of instruments to record these spectra is Shimadzu UV-1601 PC UV-Vis spectrophotometer at Chemistry Science Department, University Malaysia Terengganu. Solution of each metal complex was prepared and dilute in the solvent depending on the spectra needed.

Preparation of substituted dithiocarbazate compounds

S-benzyldithiocarbazate (SBDTC) was prepared according to the previous method that was proposed by Akbar Ali et al. in 1975. 11.4g (0.2mol) of Potassium hydroxide (KOH) is dissolve in 70ml of ethanol 90%. To this solution, 1g of hydrazine hydrate is added and the mixture is cool in an ice-salt bath to temperature 0°c. After that, 15.2g (0.2mol) carbon disulphide is added drop wise with constant stirring over an hour using mechanical stirrer. During this time, two layers are form. The lower oil layer which is light brown in colour is separate using separatory funnel and then being dissolve in 60ml of ethanol 40%at temperature below 5°cvto prevent the dithiocarbazic acid from decomposing. Then the mixture is keeps in an ice bath and 25.3g (0.2mol) of benzyl chloride is added drop wise with vigourous stirring of the mixture using a mechanical stirrer. The white product that is S-benzyldithiocarbazate (SBDTC) which formed is filter, wash with ethanol and being recrystallize after drying. The white product is keeps in a desiccator and tests its melting point. Yield : 11.85g (59.74%). Analysis calculated for SBDTC : C, 48.45%; H, 5.08%; N, 14.13%; S, 32.34%. Found : C, 47.38%; H, 4.92%; N, 12,94%; S, 31.73%. Melting Point : 130.8° C. IR (KBR): v(N-H2) 3303s, v(N-H) 3180s, v(C=S) 1047s, v(C=N) 1608s,v(N-N-C) 1344s and mixed v(C-N)(N-N) is 949s.

Preparation of schiff base

Benzyl (2E)-2- (phenylmethylidene) dithiocarbazate

The Schiff base, Benzyl(2E)-2- (phenylmethylidene)dithiocarbazate was synthesized by dissolving S-benzyldithiocarbazate, SBDTC(0.99g, 0.005mol) in hot 95% ethanol (35ml) and adding to an equimolar quantity of acetophenone (0.60ml, ≈0.005mol) also dissolved in hot 95% ethanol (20ml). The mixture was heated for 6 hours by using reflux. The mixture was then cooled to 0°C an ice salt bath for complete crystallization to occur. The product was filtered off, washed with cold ethanol, recrystallize from 95% ethanol and then dried over silica gel.

Preparation of metal complexes

Metal acetate was dissolved in 95% ethanol (40ml). Schiff base (0.2mol) was dissolved in hot 95% ethanol (40ml). The two solutions were mixed and heated on a steam bath while being stirred. Crystals formed were filtered and washed with ice cold ethanol. Some metal complexes were obtained in lower yield than others. In those cases, the reactant solution was treated with about 30ml absolute ethanol and reheated in order to concentrate the solution. The resultant solution was cooled and the solid formed was filtered and dried over silica gel. The metal salts used were copper acetate, nickel acetate tetrahydrate, cadmium acetate, cobalt acetate and zinc acetate.

Qualitative antimicrobial assay

Antimicrobial activities of the compounds were qualitatively determined by disc diffusion method (M. Akbar Ali and A.Mirza. H.,2006).A lawn of microorganisms was prepared by pipetting and evenly spreading inoculum on to agar set in petri dishes using Nutrient Agar(NA) for bacteria. Whatman No 1 filter paper disk of 6 mm diameter were impregnated with the solution of compound(mg/ml) and dried under sterile conditions. The dried disk were then placed on previously inoculated agar surface. The plates were inverted and incubated for 24 hours at 37C.Antimicrobial activity was indicated by the presence of clear inhibition zones around the disk. Commercially available penincilin, ampicilin, gentamin were used for antimicrobial control.

3. Results And Discussion.

Synthesis

In preparing SBDTC, I have found that using absolute ethanol as solvent can straight get the product rather than using ethanol 95%**.**I also have found that the synthesis of SBDTC-AP or Schiff base ligand can be carried out in refluxed for 6 hours, while for metal complexes is carried out by heating under mild heating with stirrer but not too vigorous. In preparing Co metal complexes, it could be reacted under 1:3 ratio of metal: Schiff base rather than 1:2 metal: Schiff base.

Spectroscopic Study of the Ligand Form And Its Metals Complexes

This work is basically divided into three main procedures which are first, preparing Schiff base of SBDTC, second one is preparing Schiff base ligand which is SBDTC-AP and the last one is preparing metal complexes from the selected ligand which is reacted with five transition metals to give totally five metal complexes. Compound formed was then characterized by using number of instrument and method. Among them are Fourier Transform Infra Red, UV/Vis Spectroscopy, melting point and CHNS analyzer. Structure determination was also determined by collecting crystal data from single-crystal X-ray Crystallography. And eventually, all these complexes will be tested their biological activity against selected bacteria.

Physico-Chemical Data

The physical characteristics of all complexes are shown in table in Table 1, which shows yields, colours and melting points of synthesized compounds. As we can see, metal complexes show different colours. They form many colour and paramagnetic compounds because of their partially filled shells.(Cotton F. A.,1987). Colours of products form can practically shows the reaction has slightly occurred between ligand and metal .They have higher melting point rather than Schiff base ligand. Specifically, the ligand melt at around 136.8-138.2°C .While for Co(II) ,Cu(II) ,Ni(II) ,Zn(II) and Cd(II) complexes, the melting points are 200.6-229.7°C , 217.2-247.9°C , 181.8-184.9°C, 194.1-232.4°C ,and 169.9-172.5°C respectively. Generally, all compounds had in range 1 to 5 in value, suggesting that they were relatively free of impurities. The reason is that they can involve the 3d electrons in the delocalisation as well as the 4s. The more electrons you can involve, the stronger the attractions tend to be. More over, metal complexes shows higher melting point because the metal elements itself show higher melting point due to the closed packed structure with coordination number 12. So, they have strong metallic bond and small atomic radii, thus need strong or more energy to break after coordinate through the transition metals (Chang R., 2003).Percentage yield is calculated by using this formula:

$$\% \text{ Yield} = \frac{\text{Mole of product}}{\text{Mole of Limiting Reactant}} \times 100\%$$

Limiting reactant is determined by the lowest mole must be reacted in order the reaction will be totally reacted. In forming ligand, the limiting reactant is acetophenone while in making metal complexes, limiting reactant is the ligand. As shown in table below, not all compounds were synthesized in reasonable yields.

Table 4.1-Physico Data

CHNS Analysis

Compound	Colour	Melting point	Yield (%)
SBDTC	Light yellow	129.7-130.8°C	57.00
SBDTC-Ap	Very light yellow	136.8-138.2°C	38.00
Co(SBDTC-Ap)$_3$	Greenish dark	200.6-229.7°C	30.40
Ni(SBDTC-Ap)$_2$	Brownish dark	217.2-247.9°C	52.76
Cu(SBDTC-Ap)$_2$	Black precipitate	181.8-184.9°C	36.40
Cd(SBDTC-Ap)$_2$	White precipitate	169.9-172.5°C	42.24
Zn(SBDTCAp)$_2$	White precipitate	194.1-232.4°C	51.11

CHNS Analyzer is an instrument used to calculate the percentage of carbon, sulphur, hydrogen and nitrogen elements in each compound that I have synthesized. Standard formulation for calculating percentage of elements is like below:

Percentage of the element = Σ atomic relative of element being calculated X 100%
Σ molecular relatives of all elements presence
In the compound

The CHNS elemental analyses results are in full concurrence with the empirical formulae. So the analytical data support the proposed formulation for the complexes. The values are in range of ±0.9 and above except for Zn metal complexes it is basically in range of ±5.00.This may because lack of cautious step taken in preparation of weighing the sample. It should be totally clean and less hand touched or avoid touched with bare hand at all. More over purification of the Schiff bases and metal complexes indicates that this steps was effective because there are no other molecules or even any impurities based on CHNS results. Nevertheless it is different for Zn(SBDTC-AP).3H_2O complexes. From the calculation of mass loss for this complexes, it is positively shown based on calculation indicate that loss of water molecules and this agreed with their CHNS analyses. Besides that, for inorganic compound such as metal complexes, vanadium pentoxide is added in ratio 1:2 for vanadium pentoxide: compounds to facilitate combustion occur in order to get better and precise results compared to the empirical formula. Metal complexes had a metal: ligand ratio 1:2 ratio, except for Cobalt which is 1:3(metal:ligand).

Table 4.2 Analytical data of CHNSO Analyzer

	Percentage of elements found (%)(Calc)			
Compound	C	H	N	S
SBDTC	68.3050 (69.6000)	4.8643 (4.9000)	7.0166 (7.7000)	18.1625 (17.6000)
SBDTC-AP	65.5320 (65.5000)	5.4460 (5.9600)	9.0723 (9.2700)	22.8500 (21.900)
Co(SBDTC-AP)$_3$	58.5664 (58.1377)	4.5960 (5.1854)	8.3163 (8.4764)	19.0285 (19.4019)
Cu(SBDTC-AP)$_2$	57.2871 (56.8270)	4.4999 (5.1073)	8.0954 (8.4120)	19.2275 (19.9500)
Ni(SBDTC-AP)$_2$	58.1967 (58.0930)	4.7500 (5.1798)	8.1222 (8.4498)	19.7463 (19.3800)
Zn(SBDTC-AP)$_2$	53.220 (57.5700)	4.7120 (5.1335)	7.7615 (8.3933)	17.7800 (19.2147)
Cd(SBDTC-AP)$_2$	54.7240 (53.7917)	4.3238 (4.7963)	7.0326 (7.8428)	17.6124 (17.9500)

Infrared Spectral Analysis

Fourier Transform Infra red is used to identify functional groups in each compound I have synthesized. The method used is KBR method. The results are shown in table 4.2 and 4.3. As I said before there are three classifications of methods. Firstly is SBDTC. In this compound, all peaks shows major of functional group such as *v*(NH_2),*v*(NH),*v*(C=S),*v*(C-N-N-N) and *v*(C-N) which are 3303cm-1,3180cm^{-1},1047cm^{-1},949.55cm^{-1}, and also 1608cm^{-1} respectively. Peak *v*(NH_2) at 3303cm^{-1} is not observed in ligand because its undergo deprotonation during the condensation reaction. Furthermore, this ligand does not show peak of *v*(C=O) at 1685 cm^{-1} means that the reaction produced new schiff base ligand compound which is not more starting material of carbonyl functional group in acetophenone. Confirmation of coordination to the metal through azomethine nitrogen(1) and thiolate sulphur (2) atom can be concluded based on the presence of these major functional groups as shown below.

COMPOUND	*v*(N-H_2)	*v*(N-H)	*v*(C=S)	*v*(N-N-C)	Mixed *v*(C-N), (N-N)	*v*(C=O)	*v*(C=N)
SBDTC	3303	3180	1047	1344	949.55	-	1608
Acetophenone	-	-	-	-	-	1685	-
(SBDTC)AP	-	3179.8	1103	1341	951.34	-	1599

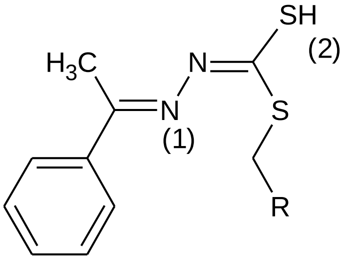


Figure 4.1 Coordination sites of NS Schiff Base.

Second one is SBDTC (AP), the peak for *v*(NH_2) is missing because hydrogen in SBDTC is deprotonated during condensation reaction forming water. SBDTC can exhibits thione-thiole tautomerisme**.** The IR spectra of the free ligand SBDTC(AP) in KBR do exhibit a *v*(C=S) band at around 1030 cm^{-1}, and show a broad band at 3179.8 cm^{-1} attributable to *v*(N-H).While for metal complexes, IR spectra show no more *v*(N-H) peak but do not exhibit a *v*(C=S) band since the thiones groups was relatively unstable in the monomeric forms and have a tendency to change into more stable thiol form by enethiolization process (Tarafder *et al.*, 2002) . However it shows *v*(C-S) band at around (916-1003)cm^{-1}. These indicate that the complexation occurred between Schiff base and metal acetate in the solid state, the ligand remains in the thione form.

Table 4.3 Infra red spectra value for SBDTC, Acetophenone and (SBDTC)AP.
SBDTC : S-benzyldithiocarbazate (SBDTC)Ap: benzyl(2*E*)-2-(phenylmethylidene)hydrazinecarbodithioate (ligand

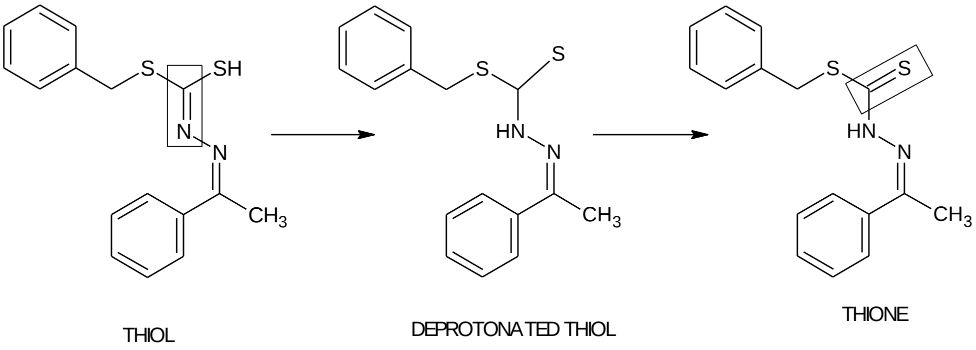


Figure 4.2 The Thiole and Thione form of the Schiff base

Although an equilibrium mixture of the thione and thiol tautomeric forms, maybe expected to exist in solution, also even in solution they can show predominantly as thione tautomers. Compound containing the thioamide (NH-C=S) functional group are capable of exhibiting thione-thiol tautomerism and therefore the acetophenone Schiff base of *S*-benzyldithiocarbazate .It can exist as thione or thiol form or as an equilibrium of both form (figure 4.2). However, previous study have shown that these ligands remain solely as thione tautomer both in the solid state as well as in solution.

The coordination of the azomethine nitrogen to the metal is indicate by the shift on the *v*(C=N) band at 1599 cm^{-1} to lower frequency .In the IR spectra of all metal complexes, the frequencies of *v*(C=N) band at were slightly affected by low electron repulsion between lone pair of N-N due to coordination of metal ion with azomethine nitrogen. Generally evidence of coordination of thiosemicarbazone and dithiocarbazate ligands to metal ions via azomethine nitrogen has been based on shifting of the azomethine (C=N) band to the the free ligand from higher to lower wavenumber in the spectra of the metal complexes (Ravoof T.H.,2006).However, shifting of this band to higher and lower wave number have been reported. The lowering of the *v*(C-S-S) band at 1027 cm^{-1} to the metal complexes proves that the Schiff base coordinates to the metal ions through one of the sulfur donors atom in the CSS group.

Table 4.4 IR results for another metal complexes compound

Wavenumber			***v*/cm^{-1}**		
Compound	***v*(NH)**	***v*(C=S)**	***v*(C-S)**	***v*(C=N)**	***v*(CSS)**
SBDTC-AP	3179.80	1103.00	-	1599.91	1027.00
Co(SBDTC-AP)$_3$	-	-	991.68	1596.02.	921.87
Ni(SBDTC-AP)$_2$	-	-	1003.00	1596.34	943.38
Cu(SBDTC-AP)$_2$	-	-	1046.05	1591.80	939.37
Zn(SBDTC-AP)$_2$	-	-	992.53	1589.85	926.82
Cd(SBDTC-AP)$_2$	-	-	996.80	1587.18	922.69

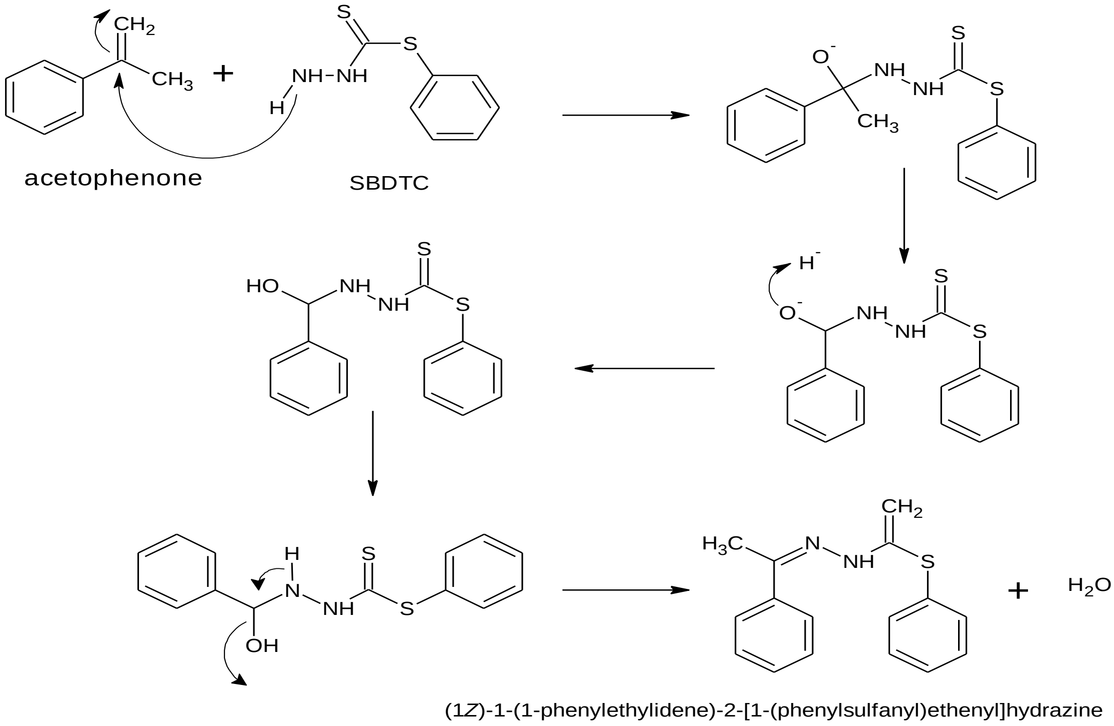


Figure 4.3 A mechanism for the formation of Dithiocarbazate Schiff bases ligand with acetophenone.

Biological activity Analysis

Target microorganisms

Four pathogenic microbials were used to test the biological potential of the complexes. They were *Aeromonas sp.,Micrococcus sp.,Staphylococcus Aurieus sp., and S. Typhy M.H s.p.* Commercially available Penicylin, Ampicyllin, and Gentamycin were used for antimicrobial control.

Antimicrobial activity

All the samples were dissolved in DMSO which is in 1mg per ml. This test is to investigate which compounds have antimicrobial potential towards selected pathogenic bacterium. For example, if the inhibitory zones for cupper complex are exceeding the standard inhibition of selected antimicrobial control, the compound is considered active. The qualitative results are shown in Table 6 .Ligand show moderately active towards three type of bacteria which are *Aeromonas, Staphylococcus sp. and S.Typhy M.H* with their antimicrobial control which are Penincillin, and Gentomicin respectively. For the series of metal complexes derived from *S*-benzyldithiocarbazate ligand SBDTC-AP it was clearly seen that after chelating, the antimicrobial activity increased, except for metal complexes that react with *S.Typhy M.H* by using gentomicin standard antimicrobial control, none of them shows positive antimicrobial activity. However, ligand schiff base show positive antimicrobial activity even though it is not exceeding inhibitory zones of gentomicin standard. Among all the metal complexes, only Zn(II) and Co(II) complexes showed weak activities against more than three types of microbes. It can be deduced that the presence of water molecules in Zn(L).3H_2O complexes has changed the biological potential of the compound.

In another antimicrobial test by *using Aeromonas, Micrococcus, and Staphylococcus aurieus* bacteria, only two out of 18 tests shows positive and exceeding the inhibitory zones of antimicrobial control which are Schiff base ligand against *Aeromonas sp.* and also Nickel complexes against *Staphylococcus aurieus* .Thus means that both are respectively shows strong activities towards selected bacteria.

Table 4.5 Quantitative assay microbial results

Compound	*Aeromonas sp.*^{a}	*Micrococcus sp*^{b}	*Staphylococcus sp.*^{c}	*S.Typhy M.**H.** sp.*^{c}
Positive control	7	22	11	11
SBDTC-AP	8	—	7	7
Co(SBDTC-AP)$_3$	6	—	—	—
Ni(SBDTC-AP)$_2$	7	—	13	—
Cu(SBDTC-AP)$_2$	8	6	—	—
Zn(SBDTC-AP)$_2$	—	8	—	—
Cd(SBDTC-AP)$_2$	7	15	11	—

Units are in millimeter
Types of positive control are in superscript representative
^{a} → Penicillin
^{b} → Ampicillin
^{c} → Gentamicin

UV Visible Analysis

Table 4.6 UV-Vis results of Schiff Base Ligand and its metal complexes.

Compounds	UV-Vis spectra (λmax, nm)
SBDTC(AP)$_2$	203,259,335
Co(L)$_3$	400,559,629,726
Ni(L)$_2$	281,375,553
Cu(L)$_2$	254,298,342,441,580
Zn(L)$_2$	255,292,333
Cd(L)$_2$	307,380

4. Conclusion

To conclude, a new Schiff Base ligand [(SBDTC)2AP] has been synthesized by the 1:2 condensation of Acetophenone and S-benzyldithiocarbazate. A group of selected ions such as Cu(II), Cd(II), Zn(II), Ni(II) and Co(II) complexes of [(SBDTC)2AP] have been prepared and characterized by elemental analysis, spectroscopic studies and various physico-chemical techniques included melting point determination, IR spectra and Uv-Vis spectra. Melting point of Schiff base is basically lower than metal complexes because of intra-molecular interaction. The FTIR spectrum for Schiff base ligand shows stretching vibration of the important functional group ;v(N-H) in range ~3179 cm-1,v(C=S) in range ~1103cm-1,v(N-N-C) in range ~1344cm-1,v(C=N) in range ~ 1599 cm-1 and lastly v(C-S-S) in range of 1027 cm-1.As for the metal complexes of Schiff base, they posses in thiol form in solid state because of the v(N-H) and v(C=S) stretching disappearance near 3179 cm-1 and 1103 cm-1 respectively. The coordination of the azomethine nitrogen and sulfur donors atom to the metal is indicate by the shift on the v(C=N) band at 1599 cm-1 and in the v(C-S-S) band at 921 cm-1 .Finally the complexes have been evaluated for their biological activities against the selected bacteria. The Schiff Base exhibits moderate activities against Staphylococcus aurieus, S.Typhy M.H. and Aeromonas sp. All metal complexes were inactive against S.Typhy M.H.

Acknowledgements

The authors would like to thank the Ministry of Higher Education Malaysia for slab slai and also my Master scholarship, from Mini Bajet 2010, Ministry of Higher Education Malaysia and Univeristi Malaysia Terengganu for providing a research place.

CHAPTER 6

BIBLIOGRAPHY

1. Ali, M.A.,Tarafdar, M.T.H.,1976. Metal complexes of sulphur and nitrogen-containing Ligands: complexes of s-benzyldithiocarbazate and A schiff base formed by its condensation with P yridine-2-carboxaldehyde *I. inorg, nucl. Chem.*,39:1785-1791
2. Ali, M.A., Mirza, A.H., Butcher, R.J., and Rahman, M. 2000. Nickel (II), copper (II), palladium (II) and platinum (II) complexes of bidentate SN ligands derived from S-alkyldithiocarbazates and the X-ray crystal structures of the [Ni(tasbz)$_2$] and [Cu(tasbz)$_2$] á CHCl3 complexes. *Transition Metal Chemistry* 25: 430-436
3. Ali, M.A., Mirza A.H., ButcherR.J.,Tarafder M.T.H., Keat. T.B. A. Manaf Ali.2002. Biological activity of palladium(II) and platinum(II) complexes of the acetone Schiff bases of *S*-methyl- and *S*-benzyldithiocarbazate and the X-ray crystal structure of the [Pd(asme)] (asme5anionic form of the 2-acetone Schiff base of *S*-methyldithiocarbazate) complex
4. Ali, M.A.,Mirza, A.H., Butcher, J.R., Crouse, K.A.,2006.The preparation ,characterization and biological activity of palladium(II) and platinum(II) complexes of tridentate NNS ligandss derived from *S*-methyldithiocarbazate and *S*-benzyldithiocarbazates and the X-Ray crystal structures of the [Pd(mpasme)Cl] complex.*Springer* 31: 79-87
5. Ali, M.A., Hjh Junaidah, A.B., Mirza, A.H., Smith, S.J., Gahan, L.R., Benhardt, P.V.2008.Preparation,spectroscopic characterization and X-Ray crystal and molecular structures of nickel(II), copper(II) and zinc(II) complexes of the Schiff base formed from isatin and *S*-methyldithiocarabazate(Hisa-sme). *Polyhedron* 27:71-79
6. Chan, M.H.E., Crouse, K.A., Tahir, M.I.M., Rosli, R., Tsafe, N.U., Cowley, A.R. 2008. Synthesis and characterization of cobalt(II), nickel(II), copper(II), zinc(II) and cadmium(II) complexes of benzyl N-[1-(thiophen-2-yl)ethylidene] hydrazine carbodithioate and benzyl N-[1-(thiophen-3-yl)ethylidene] hydrazine carbodithioate and the X-ray crystal structure of bis{benzylN-[1-(thiophen-2-yl)ethylidene] hydrazine carbodithioate}nickel(II). *Polyhedron* 27: 1141–1149
7. Chang, R. (2005). *Chemistry* (Eight ed.). New York: McGraw-Hill Companies.
8. Chew, K.B., Tarafder, M.T.H., Crouse, K.A., Ali, A.M., Yamin, B.M., and Fun, H.K. 2004. Synthesis, characterization and bio-activity of metal complexes of bidentate N–S isomeric Schiff bases derived from S-methyldithiocarbazate (SMDTC) and the X-ray structure of the bis[S-methyl-b-N-(2-furyl-methylketone) dithiocarbazato]cadmium (II) complex. *Polyhedron* 23:1385–1392.
9. Fiona, F.N.H.,Crouse, K.A.,Tahir, M.I.M,Tarafder, M.T.H, Cowley, A.R.2008. Synthesis, characterization and biological studies of S-benzyl-b-N-(benzoyl) dithiocarbazate and its metal complexes. *Polyhedron,* 27: 3325–3329.
10. Mohamed, G. G., Omar, M. M., & Hindy, A. M. (2005). Synthesis, Characterization and Biological Activity of Some Transition Metal with Schiff Base Derived from 2-thiophene Carboxaldehyde and Aminobenzoic Acid. *Spectrochimica Acta Part A* , 62 (2005) 1140-1150 Nair, M., & Joseyphus, R. S. (2007). Synthesis and Characterization of Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Tridentate Schiff Base Derived from Vanillin and DL-α-aminobutyric acid. *Spectrochimica Acta Part A* , 70 : 749-753
11. Nair, M., & Joseyphus, R. S. (2007). Synthesis and Characterization of Co(II), Ni(II), Cu(II) and Zn(II) Complexes of Tridentate Schiff Base Derived from Vanillin and DL-α-aminobutyric acid. *Spectrochimica Acta Part A* , 70 : 749-753.
12. Ravoof, T.B.S.A.,Crouse, A.K., Tahir, M.I.M., Cowley, A.R., Ali, M.A. 2007. Synthesis, characterization and bioactivity of mixed-ligand Cu(II) complexes containing S-methyldithiocarbazate derivatives and saccharinate ligands and the X-ray crystal structure of the copper–saccharinate complex containing S-methyl-b-N-(6-methylpyrid-2-yl)methylenedithiocarbazate. *Polyhedron* 23: 2491–2498

13. Rao, S.N., Kathale ,N., Rao N., Munshi,K.N.,2007. Catalytic air oxidation of olefins using molybdenum dioxo Complexes with dissymmetric tridentate O,N,S-donor Schiff base Ligands derived from o-hydroxyacetophenone and S-benzyldithiocarbazate or S-methyldithiocarbazate.*Inorganica Chimica* Acta 360 :4010–4016
14. Roy, S., Mandal, T.N., Barik, A.K., Pal, S., Gupta, S., Hazra, A., Butcher, R.J., Hunter, A.D., Zeller, M., and Kar, S.K. 2007. Metal complexes of pyrimidine derived ligands – Syntheses, characterization and X-ray crystal structures of Ni(II), Co(III) and Fe(III) complexes of Schiff base ligands derived from S-methyl/S-benzyl dithiocarbazate and 2-S-methylmercapto-6-methylpyrimidine-4-carbaldehyde. *Polyhedron* 26: 2603–2611
15. Smith, J.G. (2006). Organic Chemistry. New York: The McGraw Hill Companies.
16. Tarafder, M.T.H., Ali, M.A., Saravanan, N., Weng, Y.W., Kumar, S., Tsafe, N.U., Crouse, K.A. 2000. Coordination chemistry and biological activity of two tridentate ONS and NNS Schiff bases derived from S benzyldithiocarbazate. *Transition Metal Chemistry* 25: 295-298
17. Tarafder, M., Kasbollah, A., Crouse, K., Ali, A., Yamin, B., & Fun, H.-K. (2001). Synthesis and characterization of Zn(II) and Cd(II) complexes of *S*-benzyl-_-*N*-(2-pyridyl)methylenedithiocarbazate (HNNS): bioactivity of the HNNS Schiff base and its Zn(II), Cu(II) and Cd(II) complexes and the X-ray structure of the [Zn(NNS)2] complex. *Polyhedron* , 2363-2370.
18. Tarafder, M., Khoo, T. J., Crouse, K. A., Ali, A. M., Yamin, B. M., & Fun, H.-K. (2002). Coordination Chemistry and Bioactivity of Ni^{2+}, Cu^{2+}, Cd^{2+} and Zn^{2+} Complexes containing Bidentate Schiff Base Derived from S-benzyldithiocarbazate and the X-ray Crystal Structure of *bis*[*S*-benzyl-ß-*N*-(5-methy-2-furylmethylene)dithiocarbazato]cadmium(II). *Polyhedron* , 21 (2002) 2547-2554.
19. Zhou, H.P., Li, D.M., Wang, P., Cheng, L.H., Gao, Y.H., Zhu, Y.M., Wu, J.Y., Tian, Y.P., Tao, X.P., Jiang, M.H., and Fun, H.K. 2007. Synthesis, crystal structures, and two-photon absorption properties of dithiocarbazate Zn (II) and Pd (II) complexes. *Journal of Molecular Structure* ,826: 205–210

CHAPTER 7 APPENDICES

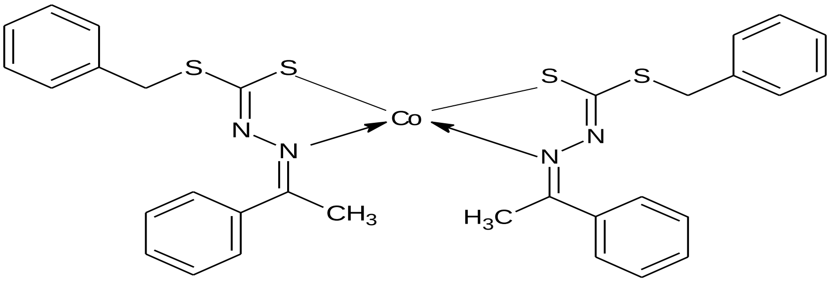


Figure 7.1 Co(L)$_2$ where L=SBDTC(AP)

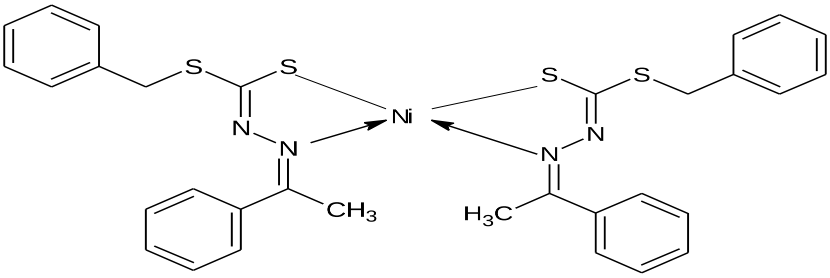


Figure 7.2 Ni(L)$_2$ where L=SBDTC(AP)

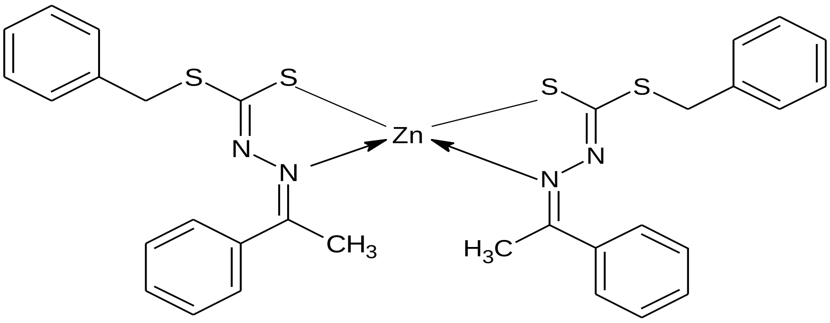


Figure 7.3 Zn(L)$_2$ where L=SBDTC(AP)

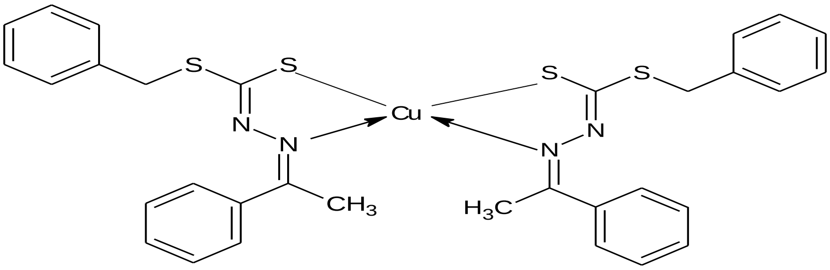


Figure 7.4 Cu(L)$_2$ where L=SBDTC(AP)

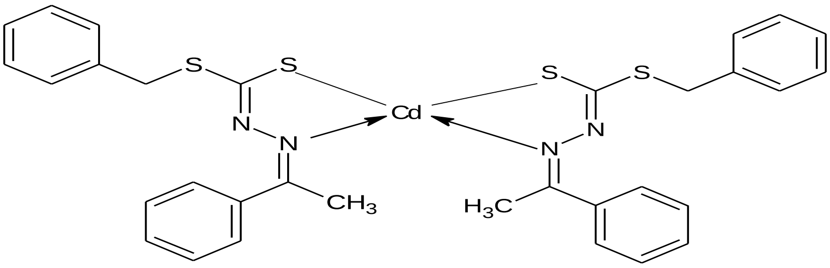


Figure 7.5 Cd(L)$_2$ where L=SBDTC(AP)

Uv-vis spectral graph

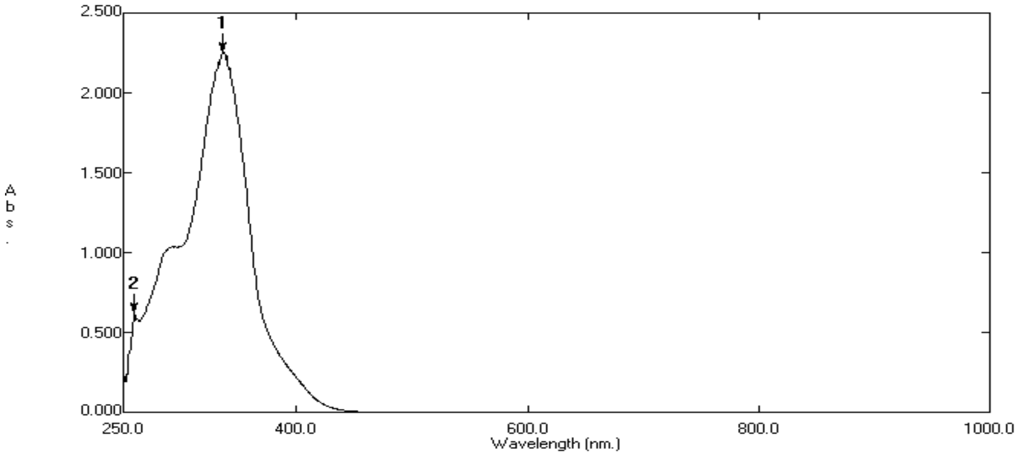


Figure 7.6. SBDTC-AP Uv-vis spectral graph

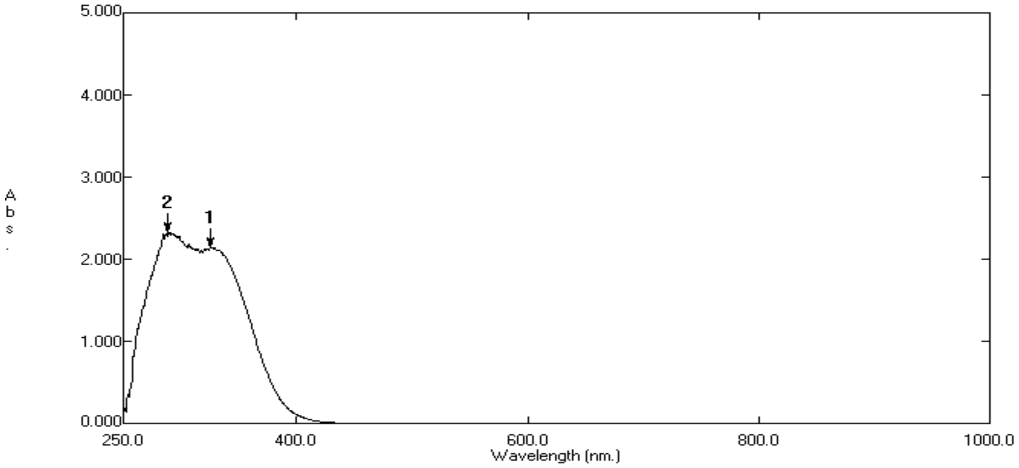


Figure 7.7. Cd(SBDTC-AP)$_2$ Uv-vis spectral graph

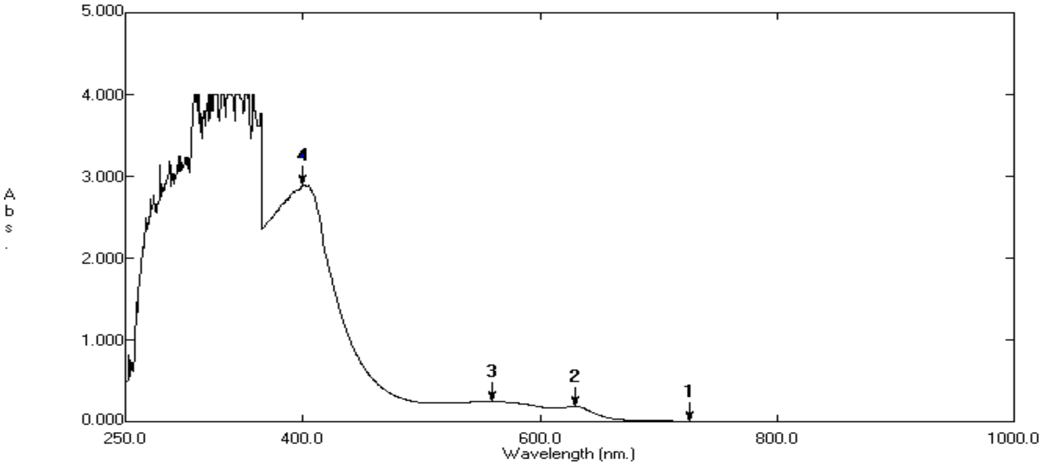


Figure 7.8 Co(SBDTC-AP)$_2$ Uv-vis spectral graph

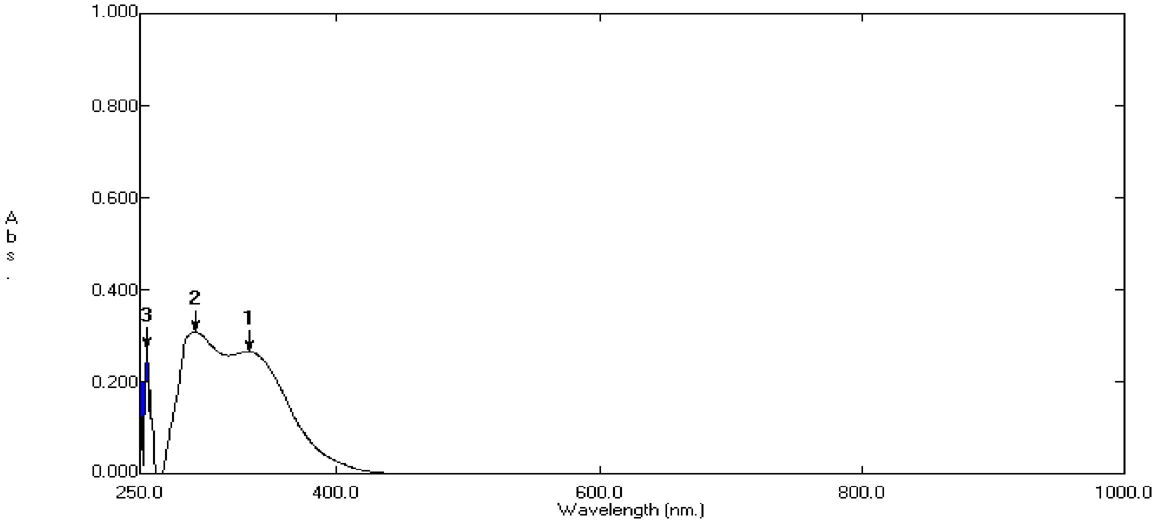


Figure 7.9. Zn(SBDTC-AP)$_2$ Uv-vis spectral graph

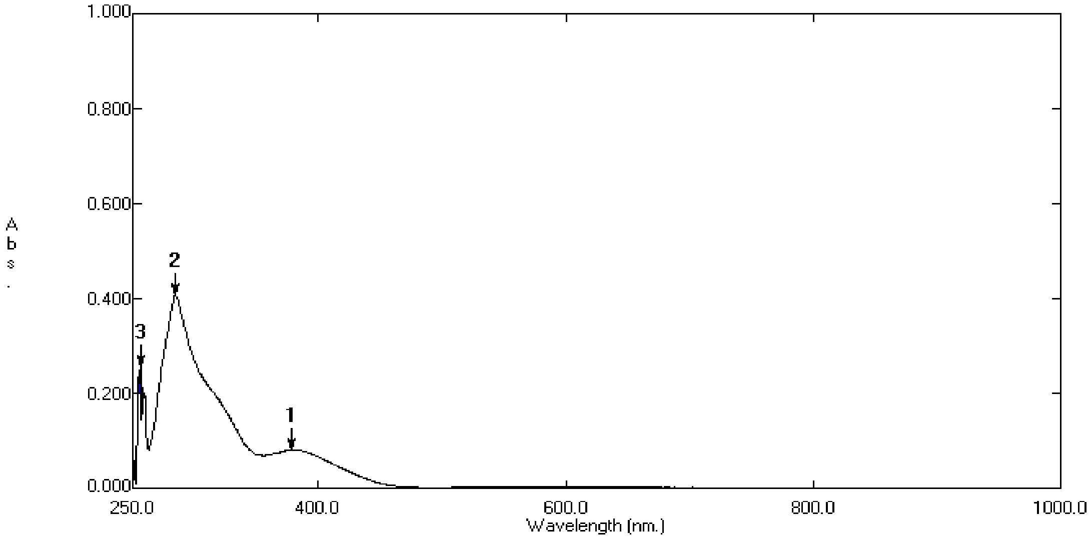


Figure 7.10 Zn(SBDTC-AP)$_2$ Uv-vis spectral graph

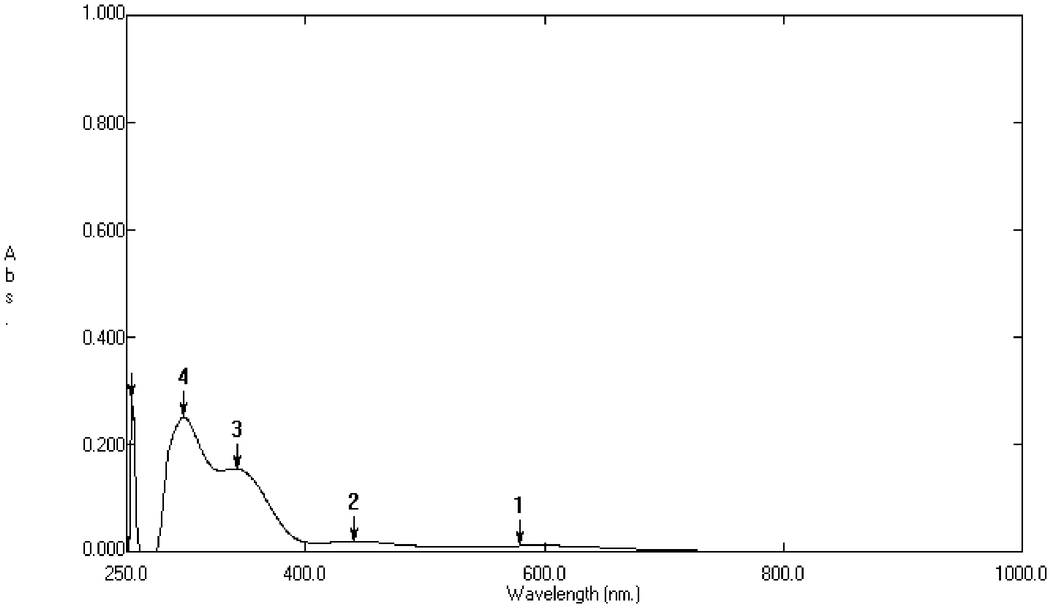


Figure 7.11. Cu(SBDTC-AP)$_2$ Uv-vis spectral graph