Borneo Journal of Resource Science and Technology (2013) 3(1): 26-34

Complexation of Bis-2-(benzylideneamino)Phenol to Cobalt(II) and Zinc(II), and their Spectroscopic Studies

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ABSTRACT

A bis-Schiff base of bis-2-(benzylideneamino)phenol (SB1) was synthesized *via* condensation reaction of terephthaldehyde and 2-aminophenol in ethanol. SB1 was then reacted with respective MX_2 salt (M = Co & Zn, X = Cl & OAc) in the ligand to metal ratio of 1:2 under refluxing condition in ethanolic KOH solution for six hours. All synthesized complexes were characterized using FT-IR and UV-vis spectroscopy. The formation of complexes with Co and Zn was indicated by the shifts observed from the IR peaks and λ_{max} of the UV absorption bands for the C=N bond. The IR peak at 1621 cm^{-1} in SB1 was shifted to around 1638 and 1619 cm^{-1} after forming its complexes with Co and Zn, respectively. The absorption band of C=N bond was blue shifted from λ_{max} of 384 nm to 307 nm in Co(II) complex, whereas this band was red-shifted to 389 nm in the Zn(II) complex. Therefore, SB1 was confirmed to coordinate with the Co(II) and Zn(II) metal centres *via* the imine nitrogen.

Keywords**:** Bis-Schiff base, Co and Zn complexation

INTRODUCTION

Schiff base is considered as a very important class of organic compounds, which is commonly employed as versatile ligands in organic and inorganic synthesis due to its wide variety of applications such as in drugs, electronic devices and catalysis applications (Nishinaga *et al*., 1988; Tarafder *et al*., 2002; Ershad *et al.,* 2009; Przybylski *et al*., 2009). Most studies of single substituted Schiff base compounds are mainly focused on the biological studies (Bagihalli *et al*., 2009; Kumar *et al*., 2010), whereas the studies of bis-Schiff base analogues are normally mainly focused on the complexation (Park *et al*, 1998; Ortiz & Park, 2000; Turan & Sekerci, 2009). However, reports on bis-2-(benzylideneamino) phenol (SB1) (Figure 1) are still very scarce especially in the complexation study with transition metals.

Most Schiff base compounds used for complexation study are bidentate in nature, and the most common one is derived from the *o*-hydroxybenzaldehyde (Park *et al*, 1998; Cotton *et al*., 1999; Ortiz & Park, 2000; Abd-Elzaher, 2001; Cozzi, 2004; Salavati-Niasari *et al*., 2005, Li *et al*., 2009). The coordination modes of this type of Schiff base ligands are usually through the nitrogen atom at the imine group and the oxygen atom from the hydroxyl at the *ortho*-position. IR spectroscopy is the most common and easiest method used for determination of the coordination mode of the complexes (Ebsworth *et al*., 1987; Crabtree, 1994; Ran *et al*., 2011). For Schiff base complexes, significant shift of the band of interest of the C=N group in IR spectrum is clearly and commonly observed.

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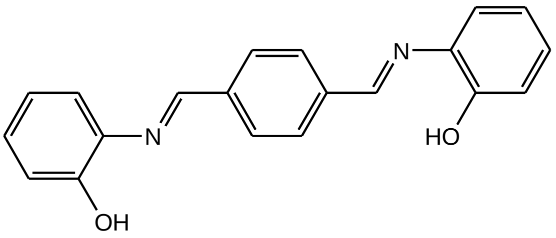


Figure 1. Structure of bis-2-(benzylideneamino)phenol (SB1)

MATERIALS & METHODS

Materials and Characterizations

Terephthaldehyde, 2-aminophenol, cobalt(II) chloride and zinc(II) acetate were obtained from Sigma Aldrich, Across and BDH, and used as received without further purification.

The infrared spectra were recorded on Perkin Elmer Spectrum GC Fourier-Transform Spectrometer using KBr disc. The ^{1}H NMR spectrum for SB1 was recorded on a JEOL ECA – 500 MHz NMR relative to TMS as the internal standard and were referenced *via* residual proton NMR resonances of the appropriate deuterated solvent (DMSO-d$_6$: δ_H 2.50). All the UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda-40-UV-Vis spectrometer with a 1 cm quartz cuvette in the range of 200 – 800 nm.

Synthesis of bis-2-(benzylideneamino) phenol (SB1)

2-aminophenol (2.18 g, 20 mmoles) and terephthaldehyde (1.34 g, 10 mmoles) were added into a beaker containing 25 mL of ethanol. The mixture was stirred at room temperature for 4 h. Yellow solid was formed, filtered and dried. The yellow solid was recrystallized *via* slow diffusion from the mixture of dichloromethane and hexane. Yield 2.83 g, 89%. m.p.: 220 – 221 °C. UV (λ_{max}, nm): 300, 384. ^{1}H NMR (DMSO-d$_6$, 500 MH$_Z$), δ_H: 9.10 (s, 1H, -OH), 8.80 (s, 1H, -CH=N-), 8.16 (s, 4H, -CH$_{arom}$), 7.26 (d, 2H, J_{H-H} = 8 Hz, CH$_{arom}$), 7.11 (t, 2H, J_{H-H} = 8 Hz, CH$_{arom}$), 6.92 (d, 2H, J_{H-H} = 8 Hz, CH$_{arom}$), 6.86 (t, 2H, J_{H-H} = 8 Hz, CH$_{arom}$). IR (KBr): υ_{OH} = 3459, $\upsilon_{C=N}$ = 1621, $\upsilon_{C=C}$ = 1582 & 1481, υ_{C-O} = 1374 cm^{-1}.

Complexation of SB1 with Co(II) and Zn(II)

General procedure

SB1 (0.032 g, 0.1 mmoles) was dissolved in 20 mL of ethanol in Schlenk round bottom flask. Potassium hydroxide (0.012 g, 0.2 mmoles) in 10 mL of ethanol was added drop wise to the SB1 solution. The colour of the mixture changed from yellow to orange. An ethanolic solution of MX$_2$ salt (0.2 mmoles) [where M = Co^{2+} and Zn^{2+}, X = Cl$^-$ and C(O)OCH$_3^-$, respectively] was added dropwise into the resulting mixture. The mixture was refluxed for 6 h and allowed to cool to room temperature. The solvent was removed *in vacuo* to afford the product.

Complexation of SB1 with Co(II), CoSB1

Cobalt(II) chloride hexahydrate (0.048 g, 0.2 mmoles). Dark brown solids, weight: 0.06 g. UV (λ_{max}, nm): 259, 307, 427. IR (KBr): ν_{O-H} = 3551, $\nu_{C=N}$ = 1638, $\nu_{C=C}$ = 1591 & 1459, ν_{C-O} = 1384, ν_{Co-N} = 584 cm^{-1}.

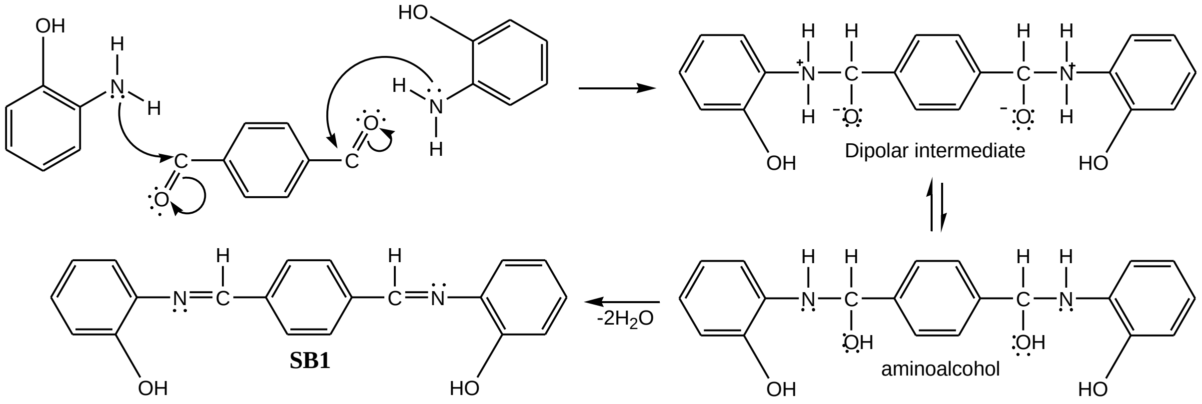
Complexation of SB1 with Zn(II), ZnSB1

Zinc(II) acetate (0.051 g, 0.2 mmoles). Reddish brown solids, weight: 0.06 g. (λ_{max}, nm): 296, 389, 475. IR (KBr): ν_{O-H} = 3414, $\nu_{C=O}$ = 1695, $\nu_{C=N}$ = 1619, $\nu_{C=C}$ = 1583 & 1472, ν_{C-O} = 1412, ν_{Zn-N} = 523 cm^{-1}.

RESULTS & DISCUSSION

Spectroscopic characterization of SB1

The yellow solid of SB1 was successfully synthesized from the reaction of terephthaldehyde with 2-aminophenol in alcoholic solution. The compound was recrystallized *via* slow diffusion from the mixture of dichloromethane and hexane to afford 89% yield. The formation of SB1 is shown in Scheme 1. Dipolar intermediate of terephthaldehyde was formed after reacting with aniline, followed by intramolecular electron rearrangement to produce aminoalcohol. SB1 was yielded through the elimination of two water molecules from aminoalcohol (Solomons & Fryhle, 2011).



Scheme 1: Mechanism of the formation of SB1

The ^{1}H NMR spectrum of SB1 is shown in Figure 2. The formation of SB1 is indicated by the presence of the C=NH resonance at δ_H 8.80 and the phenolic proton at δ_H 9.10. The four aromatic protons attributed to the middle aromatic group appeared as a singlet at δ_H 8.16.

The IR spectrum of SB1 is shown in Figure 3. The peak appeared at 1621 cm^{-1} was attributed to C=N stretching of SB1. The intra-molecular hydrogen bond between the hydroxyl group and the nitrogen atom in SB1 was observed at 3286 cm^{-1} with a broad N-H stretching band (Patel *et al.*, 2008). Indeed, this statement can be supported by a broad phenolic singlet at δ 9.10 in the ^{1}H NMR spectrum.

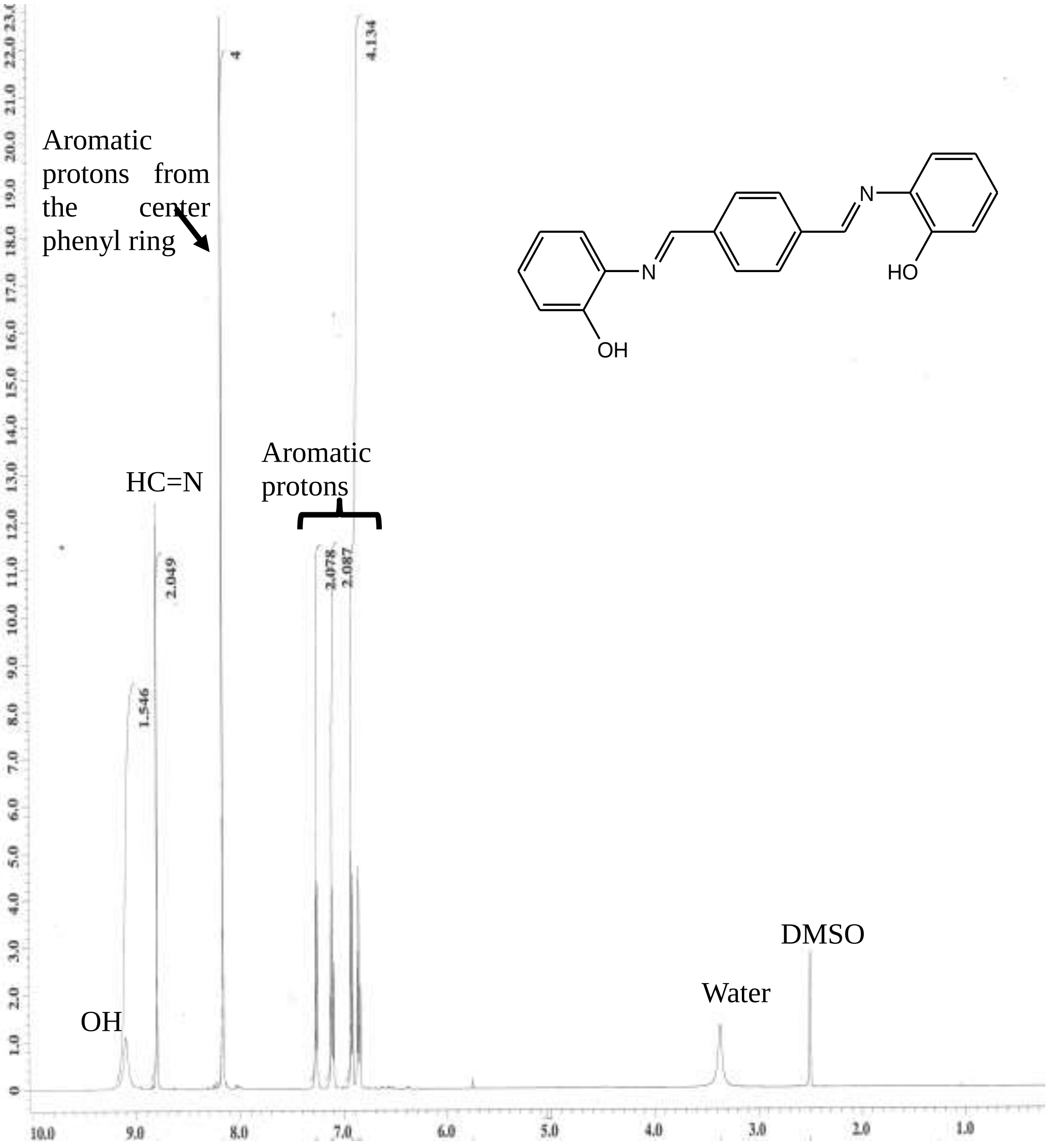


Figure 2. ^{1}H NMR spectrum of SB1

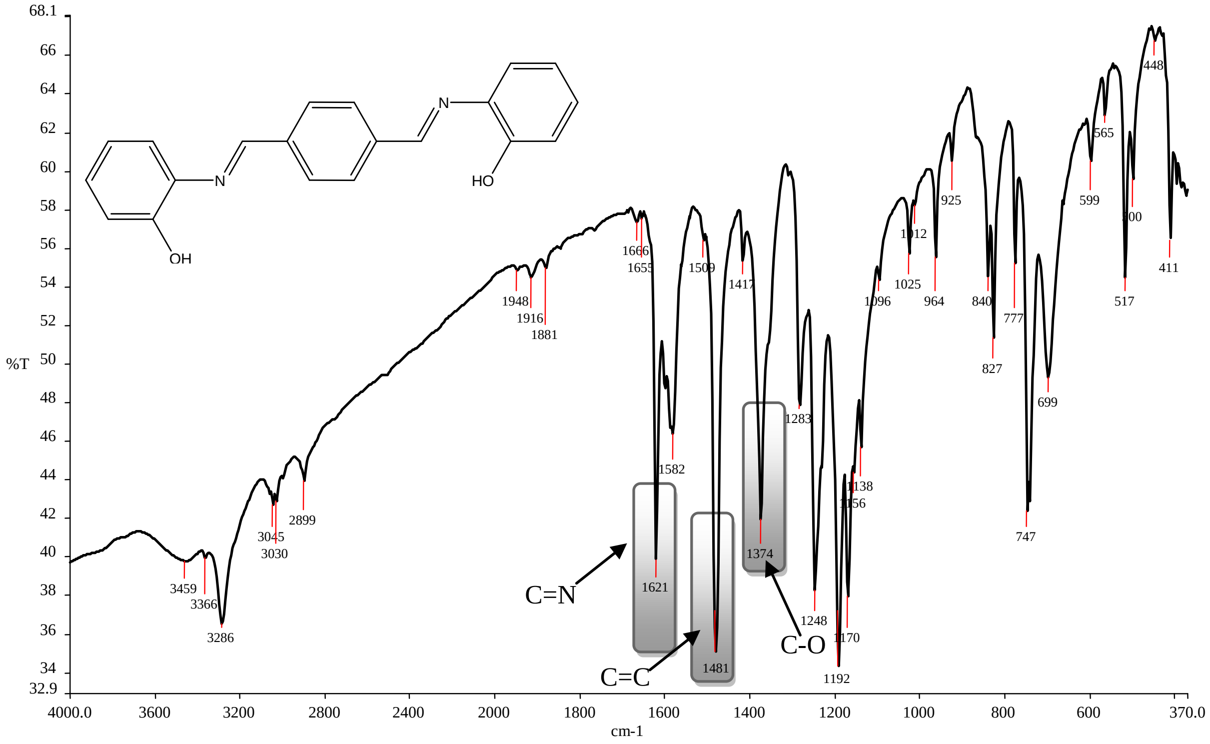


Figure 3. IR spectrum of SB1

The absorption spectrum of SB1 was recorded in DMSO at room temperature (Figure 4). Two absorption bands appeared at λ_{max} of 300 and 384 nm which are believed to be due to the π→π* transition of aromatic ring and n→π* transition of imine group, respectively.

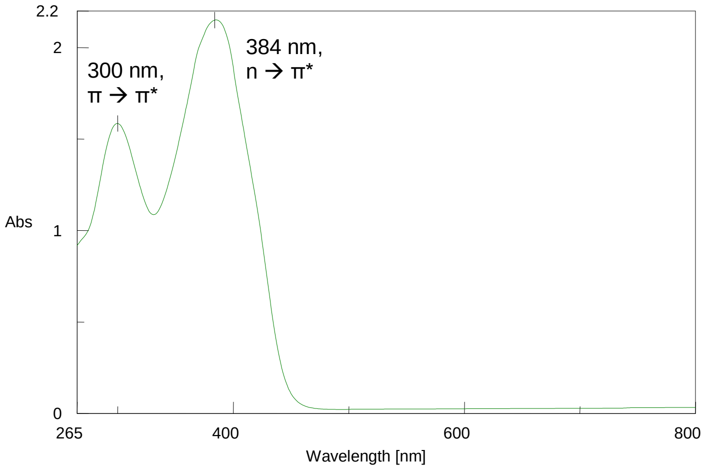


Figure 4. UV-Vis absorption spectrum of SB1

Complexation of SB1 with cobalt(II) and zinc(II)

The synthesized SB1 was reacted with cobalt(II) chloride and zinc(II) acetate, respectively, under refluxing condition for six hours. The ^{1}H NMR spectra of both complexes were not successfully obtained. For the CoSB1 complex, which was formed from the reaction of SB1 with cobalt(II) chloride, the shimming process was not responding during NMR analysis. This indicates that the Co complex is paramagnetic with the oxidation state of +2. Whereas for ZnSB1 complex which was formed from the reaction of SB1 with zinc(II) acetate, the complex was insoluble in most common NMR solvents such as DMSO-d_6 and $CDCl_3$.

However, the structural studies of both complexes were preceded with IR spectroscopy. Figure 5 shows the IR spectra of CoSB1 and ZnSB1, whereas Table 1 shows the IR data of SB1, CoSB1 and ZnSB1. For CoSB1 complex, the frequency of C=N was shifted to a higher energy at 1638 cm^{-1}, whereas for ZnSB1, the IR signal was shifted to a lower energy at 1619 cm^{-1}. The difference between the IR shifts in both complexes can be explained based on the difference of electron density in the two metals. Zinc is full with electrons in its *d* orbitals, and therefore the back-bonding from the zinc is much stronger than cobalt. The electrons back-bonded from the zinc fill up the antibonding π* orbital in C=N, and resulted a weaker bond of C=N. As a result, the C=N energy was lowered in the IR spectrum (Ray *et al*., 2011; Maity *et al*., 2011). For CoSB1, the back-bonding effect from cobalt is not as strong as zinc because cobalt exhibits much electronegative behaviour than zinc (electronegativity values: cobalt = 1.9; zinc = 1.7) and cobalt is not as electron rich as zinc. Due to high electronegativity of cobalt, the electron is withdrawn from the C=N bond to the cobalt metal centre and resulted in a stronger C=N bond. The phenolic *v*(C-O) stretching peak was observed to be shifted from 1374 cm^{-1} to 1384 cm^{-1} in CoSB1 and 1412 cm^{-1} in ZnSB1. This is due to electrons donation from oxygen to the metal centre, which simultaneously withdraws the electron from the C-O bond, resulting in an increase in the bond energy of C-O. Moreover, the additional peaks in both IR spectra at 584 and 523 cm^{-1} in CoSB1 and ZnSB1, respectively, were attributed to *v*(M-N), which therefore support the formation of both complexes (Bhattacharjee *et al*., 2012). The OH absorption band found at the region of 3413 to 3448 cm^{-1} is believed to be due to the presence of water vapour from the surrounding environment during the IR analysis.

Table 1: IR data (cm^{-1}) of SB1, CoSB1 and ZnSB1

Compounds	***v*(C=O)**	***v*(C=N)**	***v*(C=C)**	***v*(C-O)**	***v*(M-N)**
SB1	-	1621	1582, 1481	1374	-
CoSB1	-	1638	1591, 1459	1384	584
ZnSB1	1695	1619	1583, 1472	1412	523

Key: “-“ indicates no data.

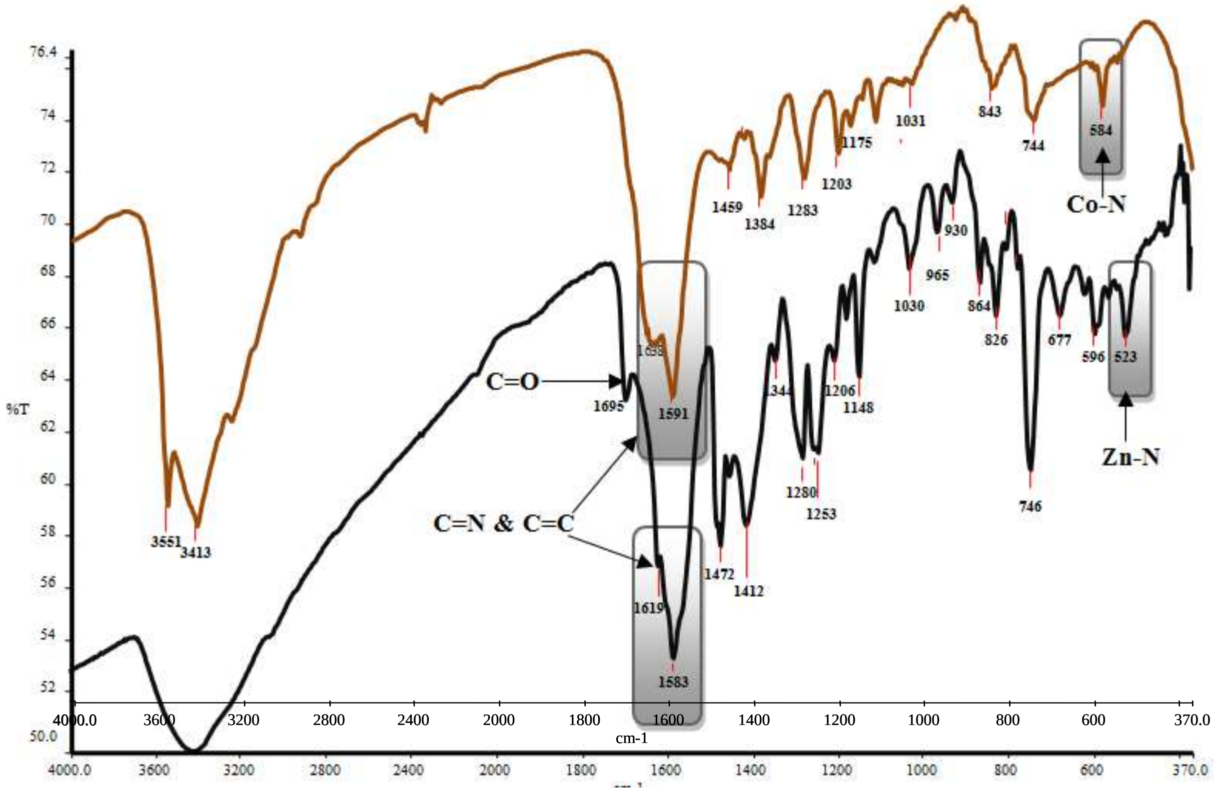


Figure 5. IR spectra of CoSB1 (top) and ZnSB1 (bottom)

The UV absorption spectra of CoSB1 and ZnSB1 were recorded in DMSO at room temperature (Figure 6). For CoSB1, the n→π* absorption band of C=N group was blue shifted to a shorter wavelength at 307 nm, whereas the ZnSB1 complex showed bathochromic shift to longer wavelength at 389 nm compared to SB1 (384 nm). These absorption bands shifts support the IR results where the C=N was strengthened in CoSB1 but it was weaken in ZnSB1. Both complexes exhibited an additional absorption band at 427 nm for CoSB1 and 475 nm for ZnSB1. This may be due to a metal-to-ligand charge transfer (MLCT) in the complex (Ran *et al*., 2011).

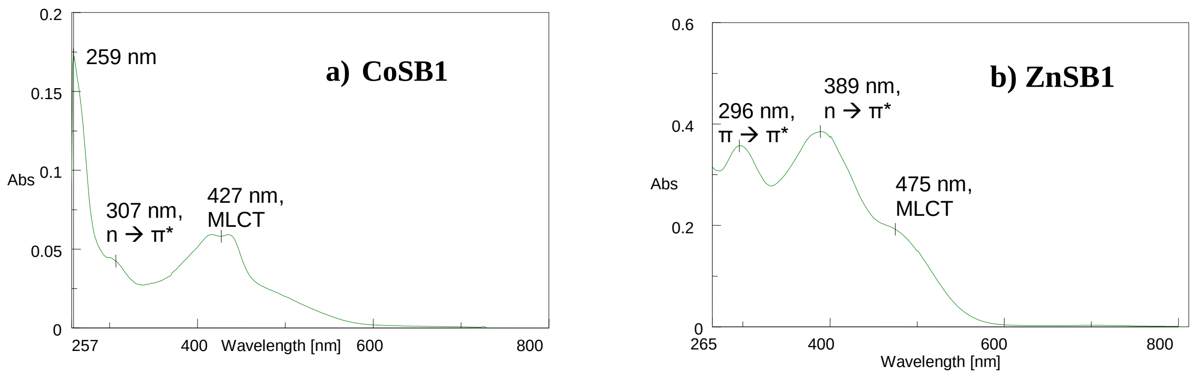


Figure 6. UV-Vis spectra of a) CoSB1 and b) ZnSB1

CONCLUSION

SB1 successfully formed complexes with cobalt and zinc, respectively. Significant shifts were observed in the IR and UV spectra after the complexation reactions. Based on the IR results, the coordination of SB1 to the respective metal centers was confirmed to be *via* the imine nitrogen.

ACKNOWLEDGMENTS

We are grateful to the Ministry of Higher Education, Malaysia for the financial support through research grant FRGS/02(27)/770/2010(51).

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