

Synthesis, Structural Characterization and DPPH Radical Scavenging Activity of Cu(II), Ni(II), Zn(II) and Cd(II) Complexes of 2,6-diacetylpyridine bis(benzenesulfonohydrazide)

Sintesis, Pencirian Struktur dan Aktiviti Pemerangkap Radikal DPPH bagi Kompleks Cu(II), Ni(II), Zn(II) dan Cd(II) 2,6-diasetilpiridinbis(benzensulfonohidrazida)

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Abstract

Cu(II), Ni(II), Zn(II) and Cd(II) complexes were synthesized from 2,6-Diacetylpyridine bis(benzenesulfonohydrazide) ligands; DAP(BSH)₂, DAP(CH₃BSH)₂ and DAP(OCH₃BSH)₂. All complexes were characterized using IR and UV-Vis spectroscopic techniques. The IR spectra revealed the disappearance of $\nu(\text{N-H})$ absorption band, which suggests that the proton on the imine nitrogen atom of the ligand was deprotonated upon complexation. The involvement of sulfonyl oxygen atoms in the coordination was evident by the absence of $\nu_{\text{as}}(\text{SO}_2)$ absorption bands. This was further confirmed by the appearance of SO₂ bending vibration band, which suggests the distortion of SO₂ from its structure. The antioxidant activity of the complexes was determined by their DPPH radical scavenging activity. The result showed that the DPPH radical scavenging activity of the parent ligands was reduced when they were chelated with Cu(II), Ni(II), Zn(II) and Cd(II) ions. Of the complexes studied, Zn(II) complexes of DAP(BSH)₂ and DAP(OCH₃BSH)₂ exhibited better antioxidant activity.

Keywords complexes, 2,6-Diacetylpyridine bis(benzenesulfonohydrazide), antioxidant, DPPH radical scavenging activity

Abstrak

Kompleks Ni(II), Zn(II) dan Cd(II) telah disintesis daripada ligan 2,6-Diasetilpiridin bis(benzensulfonohidrazida); DAP(BSH)₂, DAP(CH₃BSH)₂ dan DAP(OCH₃BSH)₂. Semua sebatian kompleks tersebut telah dilakukan pencirian menggunakan teknik spektroskopi IR dan UV-Vis. Jalur penyerapan $\nu(\text{N-H})$ pada spektra IR yang hilang menunjukkan atom nitrogen pada kumpulan imin telah dinyahproton semasa pembentukan kompleks. Penglibatan atom oksigen dari kumpulan sulfonil dalam proses koordinatan telah dibuktikan dengan kehilangan jalur penyerapan $\nu_{\text{as}}(\text{SO}_2)$. Keadaan ini disahkan lagi dengan kemunculan jalur penyerapan bagi bengkokan kumpulan SO₂, iaitu kesan herotan SO₂ daripada strukturnya. Aktiviti antioksidan bagi kompleks ditentukan melalui

keputusan aktiviti sebagai pemerangkap radikal DPPH. Hasil kajian mendapati aktiviti pemerangkapan radikal DPPH bagi ligan telah berkurangan apabila berlaku pengkelatan dengan ion Cu(II), Ni(II), Zn(II) dan Cd(II). Kompleks Zn(II) daripada DAP(BSH)₂ dan DAP(OCH₃BSH)₂ mempamerkan aktiviti antioksidan yang lebih baik berbanding dengan kompleks-kompleks lain.

Kata kunci kompleks, 2,6-Diasetilpiridin bis(benzensulfonohidrazida), antioksidan, aktiviti pemerangkap radikal DPPH

Introduction

Sulfonamides such as aromatic sulfonamides represent the most important class of biologically active compounds, which can serve as useful therapeutic agents for treating numerous diseases, including glaucoma, cancer and obesity (Özdemir *et al.*, 2010). Sulfonyl hydrazones, derivatives of sulfonamide, also exhibit various biological activities especially in medicinal applications. 4-substituted benzenesulfonylhydrazones were found to be active against certain bacteria such as *Streptococcus pyogenes* and *E. coli* (Zimmer *et al.*, 1959), while N-arylsulfonyl hydrazones have been identified as novel inhibitors of IMP-1 a metallo- β -lactamase enzyme (Siemann *et al.*, 2002).

The potentially effect of the compounds inhibiting the variety of diseases are generally attributed to their ability as free radical scavengers in biological systems or antioxidant. The chain reactions which are initiated by reactive oxygen species (ROS) such as singlet oxygen, superoxide anion, hydrogen peroxide, hydroxyl radicals, hypochlorous acid and nitric oxide radicals to modify lipids, proteins and DNA that damage cells could terminated by the presence of antioxidant (Sies, 1997). Therefore, research on natural antioxidants, as well as synthetic antioxidants is important.

It is known that coordination sulfonamides with metals can modify the pharmacological properties and toxicology of free sulfonamide (Blasco *et al.*, 1996). Research has further investigated by synthesizing metal complexes of other sulfonamide analogues such as sulfonylhydrazones to improve the understanding of their biological activity and enhance the abilities to predict new drugs (Bult *et al.*, 1983). As discussed by Xi *et al.* (2009) and Qin *et al.* (2009), the ability of an organic ligand to act as free radical acceptor can be increased when it is co-coordinated with suitable metal ion.

To our best knowledge, there is no study on 1, 1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activity of 2,6-diacetylpyridinebis(benzenesulfonylhydrazide) has been reported. This paper describes the synthesis of Cu(II), Ni(II), Zn(II) and Cd(II) transition metal complexes bearing 2,6-diacetylpyridinebis(benzenesulfonylhydrazide) ligand, and their characterization, as well as the study on their (DPPH) radical scavenging activity. The free radical DPPH (DPPH•) assay was chosen due its ability to accommodate a large number of samples in a short period and is sensitive enough to detect compounds at low concentrations.

Experimental

Materials and measurements

2,6-diacetylpyridine, benzenesulfonohydrazine, 4-methylbenzenesulfonohydrazine and 4-methoxybenzenesulfonohydrazine were purchased from Aldrich-Sigma. Ethanol was

distilled prior to use. All chemicals were of analytical grades and used without any further purification. Magnetic susceptibility was measured with a Sherwood Scientific MSB-AUTO magnetic susceptibility balance at 298 K. Diamagnetic corrections were applied using Pascal's constants. The IR spectra were recorded on a Perkin-Elmer RX1 FTIR spectrometer in the range of 400-4000 cm^{-1} at room temperature. Samples were prepared as KBr pellets. The electronic spectra were measured by means of a Shimadzu 1601 spectrophotometer in the region 200-1100 nm.

Preparation of Complexes

General method for preparation of Ni(II), Zn(II) and Cd(II) complexes

The following nine complexes were prepared by the addition of ethanolic solution containing a stoichiometric amount of hydrated nickel(II) acetate, zinc(II) acetate or cadmium(II) acetate as outlined by Yusnita *et al.* (2009a). The resultant white or yellow precipitates were filtered, washed with cold ethanol and dried under vacuum (Yield: 51-58%). Dimethylsulfoxide and pyridine identified as the most suitable solvents were used for all the complexes. The crystals of $[\text{NiDAP}(\text{BSH})_2(\text{py})_2]$ for single crystal X-ray diffraction analysis were successfully recrystallized and has been published elsewhere (Yusnita *et al.*, 2010).

$\text{NiDAP}(\text{BSH})_2 \cdot 2\text{H}_2\text{O}$

Melting point: 245°C. Anal. Calc. For $\text{C}_{21}\text{H}_{23}\text{N}_5\text{O}_6\text{S}_2\text{Ni}$: C, 44.69; H, 4.12; N, 12.41%. Found: C, 44.49; H, 4.22; N, 12.24%. IR [ν_{max} (cm^{-1}) (KBr)]: ν_{OH} 3435; $\nu_{\text{C=N}}$ 1596; $\nu_{\text{s}}(\text{SO}_2)$ 1171; $\nu_{\text{dis}}(\text{SO}_2)$ 1090; UV-Vis [λ_{max} (nm) (DMSO)]: 305 ($\pi \rightarrow \pi^*$); 330 ($n \rightarrow \pi^*$); 420 (LMCT), 680 (d-d transition). $\mu_{\text{eff}} = 3.08$ BM.

$\text{NiDAP}(\text{CH}_3\text{BSH})_2 \cdot 2\text{H}_2\text{O}$

Melting point: 275°C. Anal. Calc. For $\text{C}_{23}\text{H}_{29}\text{N}_5\text{O}_6\text{S}_2\text{Ni}$: C, 46.63; H, 4.60; N, 11.83%. Found: C, 46.45; H, 4.81; N, 11.62%. IR [ν_{max} (cm^{-1}) (KBr)]: ν_{OH} 3368; $\nu_{\text{C=N}}$ 1595; $\nu_{\text{s}}(\text{SO}_2)$ 1154; $\nu_{\text{dis}}(\text{SO}_2)$ 1083; UV-Vis [λ_{max} (nm) (DMSO)]: 315 ($\pi \rightarrow \pi^*$); 335 ($n \rightarrow \pi^*$); 410 (LMCT), 679 (d-d transition). $\mu_{\text{eff}} = 3.10$ BM.

$\text{NiDAP}(\text{OCH}_3\text{BSH})_2 \cdot 2\text{H}_2\text{O}$

Melting point: 251°C. Anal. Calc. For $\text{C}_{23}\text{H}_{29}\text{N}_5\text{O}_8\text{S}_2\text{Ni}$: C, 44.24; H, 4.37; N, 11.22%. Found: C, 44.43; H, 4.62; N, 10.90%. IR [ν_{max} (cm^{-1}) (KBr)]: ν_{OH} 3475; $\nu_{\text{C=N}}$ 1592; $\nu_{\text{s}}(\text{SO}_2)$ 1154; $\nu_{\text{dis}}(\text{SO}_2)$ 1081; UV-Vis [λ_{max} (nm) (DMSO)]: 255 ($\pi \rightarrow \pi^*$); 330 ($n \rightarrow \pi^*$); 425 (LMCT), 679 (d-d transition). $\mu_{\text{eff}} = 3.07$ BM.

$\text{ZnDAP}(\text{BSH})_2 \cdot 2\text{H}_2\text{O}$

Melting point: 225°C. Anal. Calc. For $\text{C}_{21}\text{H}_{23}\text{N}_5\text{O}_6\text{S}_2\text{Zn}$: C, 44.17; H, 4.07; N, 12.27%. Found: C, 44.05; H, 4.09; N, 11.85%. IR [ν_{max} (cm^{-1}) (KBr)]: ν_{OH} 3433; $\nu_{\text{C=N}}$ 1586; $\nu_{\text{s}}(\text{SO}_2)$

1156; $\nu_{\text{dis}}(\text{SO}_2)$ 1075; UV-Vis [λ_{max} (nm) (DMSO)]: 305 ($\pi \rightarrow \pi^*$); 315 ($n \rightarrow \pi^*$); 410 (LMCT).
 μ_{eff} = diamagnetic

ZnDAP(CH₃BSH)₂•2CH₃OH

Melting point: 232°C. Anal. Calc. For C₂₅H₃₁N₅O₆S₂Zn: C, 44.87; H, 4.99; N, 11.17%. Found: C, 47.79; H, 5.17; N, 11.33%. IR [ν_{max} (cm⁻¹) (KBr)]: ν_{OH} 3393; $\nu_{\text{C=N}}$ 1598; $\nu_{\text{s}}(\text{SO}_2)$ 1149; $\nu_{\text{dis}}(\text{SO}_2)$ 1085; UV-Vis [λ_{max} (nm) (DMSO)]: 315 ($\pi \rightarrow \pi^*$); 335 ($n \rightarrow \pi^*$); 410 (LMCT).
 μ_{eff} = diamagnetic

[ZnDAP(OCH₃BSH)₂•2H₂O]•H₂O

Melting point: 214°C. Anal. Calc. For C₂₃H₃₁N₅O₉S₂Ni: C, 42.56; H, 4.51; N, 10.79%. Found: C, 42.78; H, 4.82; N, 10.63%. IR [ν_{max} (cm⁻¹) (KBr)]: ν_{OH} 3523; $\nu_{\text{C=N}}$ 1597; $\nu_{\text{s}}(\text{SO}_2)$ 1152; $\nu_{\text{dis}}(\text{SO}_2)$ 1090; UV-Vis [λ_{max} (nm) (DMSO)]: 255 ($\pi \rightarrow \pi^*$); 325 ($n \rightarrow \pi^*$); 405 (LMCT).
 μ_{eff} = diamagnetic

CdDAP(BSH)₂•2CH₃OH

Melting point: 280°C. Anal. Calc. For C₂₃H₂₉N₅O₆S₂Cd: C, 42.89; H, 3.92; N, 10.89%. Found: C, 42.96; H, 3.71; N, 11.52. IR [ν_{max} (cm⁻¹) (KBr)]: ν_{OH} 3449; $\nu_{\text{C=N}}$ 1588; $\nu_{\text{s}}(\text{SO}_2)$ 1156; $\nu_{\text{dis}}(\text{SO}_2)$ 1085; UV-Vis [λ_{max} (nm) (DMSO)]: 300 ($\pi \rightarrow \pi^*$); 319 ($n \rightarrow \pi^*$); 400 (LMCT).
 μ_{eff} = diamagnetic

CdDAP(CH₃BSH)₂•2CH₃OH

Melting point: 283°C. Anal. Calc. For C₂₅H₃₅N₅O₆S₂Cd: C, 44.67; H, 4.36; N, 10.42%. Found: C, 44.59; H, 4.12; N, 10.97%. IR [ν_{max} (cm⁻¹) (KBr)]: ν_{OH} 3409; $\nu_{\text{C=N}}$ 1587; $\nu_{\text{s}}(\text{SO}_2)$ 1156; $\nu_{\text{dis}}(\text{SO}_2)$ 1065; UV-Vis [λ_{max} (nm) (DMSO)]: 315 ($\pi \rightarrow \pi^*$); 300 ($n \rightarrow \pi^*$); 405 (LMCT).
 μ_{eff} = diamagnetic

CdDAP(OCH₃BSH)₂•2CH₃OH

Melting point: 279°C. Anal. Calc. For C₂₅H₃₅N₅O₈S₂Cd: C, 42.64; H, 4.16; N, 9.95%. Found: C, 42.89; H, 3.94; N, 10.63%. IR [ν_{max} (cm⁻¹) (KBr)]: ν_{OH} 3448; $\nu_{\text{C=N}}$ 1588; $\nu_{\text{s}}(\text{SO}_2)$ 1153; $\nu_{\text{dis}}(\text{SO}_2)$ 1070; UV-Vis [λ_{max} (nm) (DMSO)]: 255 ($\pi \rightarrow \pi^*$); 320 ($n \rightarrow \pi^*$); 405 (LMCT).
 μ_{eff} = diamagnetic

1, 1-diphenyl-2-picrylhydrazyl (DPPH) Radical Scavenging Activity

The antioxidant activity of the new compounds was determined using DPPH radical. DPPH was stable with a purple color and has a maximum absorption (Abs.) at 517 nm. The free radical-scavenging assay was based on the discoloration of the compound when reduced by a free radical scavenger. A volume of 5 μL of each compound (with a concentration range 0.078-10.0 mg/mL) was added to 195 μL of DPPH solution (100 μM) in a test tube and shaken vigorously. After incubation at 37°C for 35 min in the dark, the absorbance of

each solution was determined at 517 nm against a blank sample containing only DPPH as negative control. The free-scavenging activity was expressed as percentage scavenging of DPPH by the chemical synthesis and was calculated as follows:

$$\text{DPPH radical - scavenging activity (\%)} = \frac{\text{Abs. blank} - \text{Abs. sample}}{\text{Abs. blank}} \times 100$$

Each test was carried out in triplicate. The total free radical scavenging capacity of the compounds was compared to vitamin C, used as standard.

Results and Discussion

General characterization

Infrared spectra

The IR spectra for the series of DAP(BSH)₂ Schiff base ligands and their copper complexes have been discussed previously (Yusnita *et al.*, 2009a). The IR spectra for all Ni(II), Zn(II) and Cd(II) complexes of DAP(BSH)₂ display a similar trend to that of reported in [ZnDAP(BSH)₂(dmsO)₂] by Yusnita *et al.* (2009b). The absence of $\nu(\text{N-H})$ absorption band of the free ligand suggests that the proton on the NH group of the ligand disappeared upon complexation (Sousa *et al.*, 2001). Coordination of the azomethine nitrogen to metal ion is indicated by the shift of the $\nu(\text{C=N})$ of the free ligand to lower energy. Additionally, it was reported that the coordination of the azomethine nitrogen atom to the metal(II) ion can be also indicated by the displacement of the band chiefly assigned to the $\nu(\text{N-N})$ stretching vibration (Akbar Ali *et al.*, 2003). The spectra of all complexes exhibit upward shifts of $\nu(\text{N-N})$ from 1072-1092 cm⁻¹ for ligands to 1118-1134 cm⁻¹ region which attributed typical

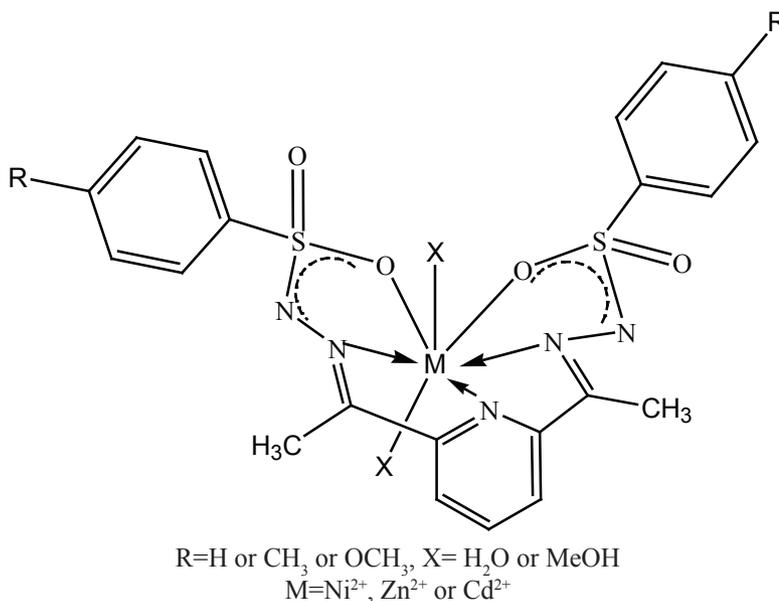


Figure 1 Proposed structure for Nickel(II), Zinc(II) and Cadmium(II) complexes of DAP(BSH)₂

coordination of the ligands to the metal ion through the azomethine nitrogen atom (Mohan *et al.*, 1985). Furthermore it was confirmed by the appearance of a new signal at 596-605 cm^{-1} region which can be attributed for M-N vibration (Abdel-Latif *et al.*, 2007).

The complexes show the disappearance signal of $\nu_{\text{as}}(\text{SO}_2)$ band at 1327-1341 cm^{-1} and the shift of $\nu_{\text{s}}(\text{SO}_2)$ to lower frequency suggesting the involvement of sulfonyl oxygen during the complexation to metal ion (González-Álvarez *et al.*, 2004). This is further confirmed by the appearance of a new band at 1077-1090 cm^{-1} region, which assigned to the bending SO_2 group suggests the distortion of the SO_2 from its structure (Rakha *et al.*, 1989). The IR spectra is very useful in assigning the metal atom which was chelated by dianionic pentadentate Schiff base *via* the two azomethine N atoms, two sulfonyl O and pyridine N atom as shown in Figure 1. This feature is similar to those $[\text{ZnDAP}(\text{BSH})_2(\text{dmsO})_2]$ and $[\text{NiDAP}(\text{BSH})_2(\text{py})_2]$ complexes which have been proven by the X-Ray structure previously (Yusnita *et al.*, 2009(b); Yusnita *et al.*, 2010).

The coordinated water molecule is indicated by a broad band in the region 3448-3488 cm^{-1} . This feature was similar to those reported in other complexes of 1,2,3-triazole Schiff bases as discussed by Bagihalli *et al.* (2008). Furthermore the coordinated water molecule due to $\nu(\text{-OH})$ rocking and wagging mode vibrations was reported in nickel(II) and copper(II) complexes of 2,6-diacetylpyridine bis(carbohydrazone) as two weaker bands at 815-816 and 612-618 cm^{-1} (Chandra & Sharma, 2009). However only one of the bands can be assigned at 803-809 due the overlapping of $\nu(\text{M-N})$ signal in the region 597-600 cm^{-1} .

Absorption spectra and magnetic studies

The $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the spectra of the ligands which is associated with azomethine chromophore and aromatic rings have been discussed previously (Yusnita *et al.*, 2009a). The electronic spectra of Ni(II) in the series of $\text{DAP}(\text{BSH})_2$ exhibit new bands at 405-415 nm (24,691-24,096 cm^{-1}) associated to intra ligand charge transfer (LMCT). In addition, the shifting band of $n \rightarrow \pi^*$ transition with 20-30 nm is of a higher wavelength from their free ligand. Both of these features occurred corresponding to the coordination of the ligand $\text{DAP}(\text{BSH})_2$, $\text{DAP}(\text{CH}_3\text{BSH})_2$ and $\text{DAP}(\text{OCH}_3\text{BSH})_2$ with Ni(II) ions. The presence of absorption bands were shown as a shoulder occurring at 679-680 nm attributed to d-d transitions, hence further support the bonding of the ligands to Ni(II) ion. The d-d band spectra of $\text{NiDAP}(\text{BSH})_2$, $\text{NiDAP}(\text{CH}_3\text{BSH})_2$ and $\text{NiDAP}(\text{OCH}_3\text{BSH})_2$ were comparable to those of seven coordinate pentagonal bipyramid complexes of $[\text{NiL}^8(\text{OH}_2)_2]$ $[\text{NO}_3]_2 \cdot \text{H}_2\text{O}$ (Cairns *et al.*, 1979) and $[\text{NiL}^1][\text{BPh}_4]_2$ (Drew *et al.*, 1981); two bands occurred at 727 nm (13,750 cm^{-1}) and 1,538 nm (6,500 cm^{-1}).

Zinc(II) and Cadmium(II) complexes were diamagnetic as expected for d^{10} configuration. The bathochromic shifts in $n \rightarrow \pi^*$ transition for Zn(II) and Cd(II) complexes were showed significantly. It is clear that a new band was observed with strong intensity at 400-410 nm or 25,000-24,390 cm^{-1} , which could be assigned to charge transfer band. No d-d transition was observed in the spectrum of Zinc(II) and Cadmium(II) complexes due to the fully occupied orbital of the metal ion (Majumder *et al.*, 2006). The absence of d-d bands is similar to those reported in Zn(II) and Cd(II) complexes of 2,6-diacetylpyridine bis(²N-methylthiosemicarbazone) (Akbar Ali *et al.*, 2006) and Cd(II) complexes of 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone) (Gudasi *et al.*, 2006) which are found to have diamagnetic character and pentagonal bipyramid structure. Therefore, the electronic

spectra and magnetic character of the present complexes helped in assigning their definite structures.

1, 1-diphenyl-2-picrylhydrazyl (DPPH) Radical Scavenging Activity

The antioxidant activities of the series DAP(BSH)₂ ligands and their Cu(II), Ni(II), Zn(II) and Cd(II) complexes were compared as percentage of DPPH radical scavenging and presented in Figure 2. The value of IC₅₀ was not evaluated due the low antioxidant activity resulted from the parent ligands and their complexes.

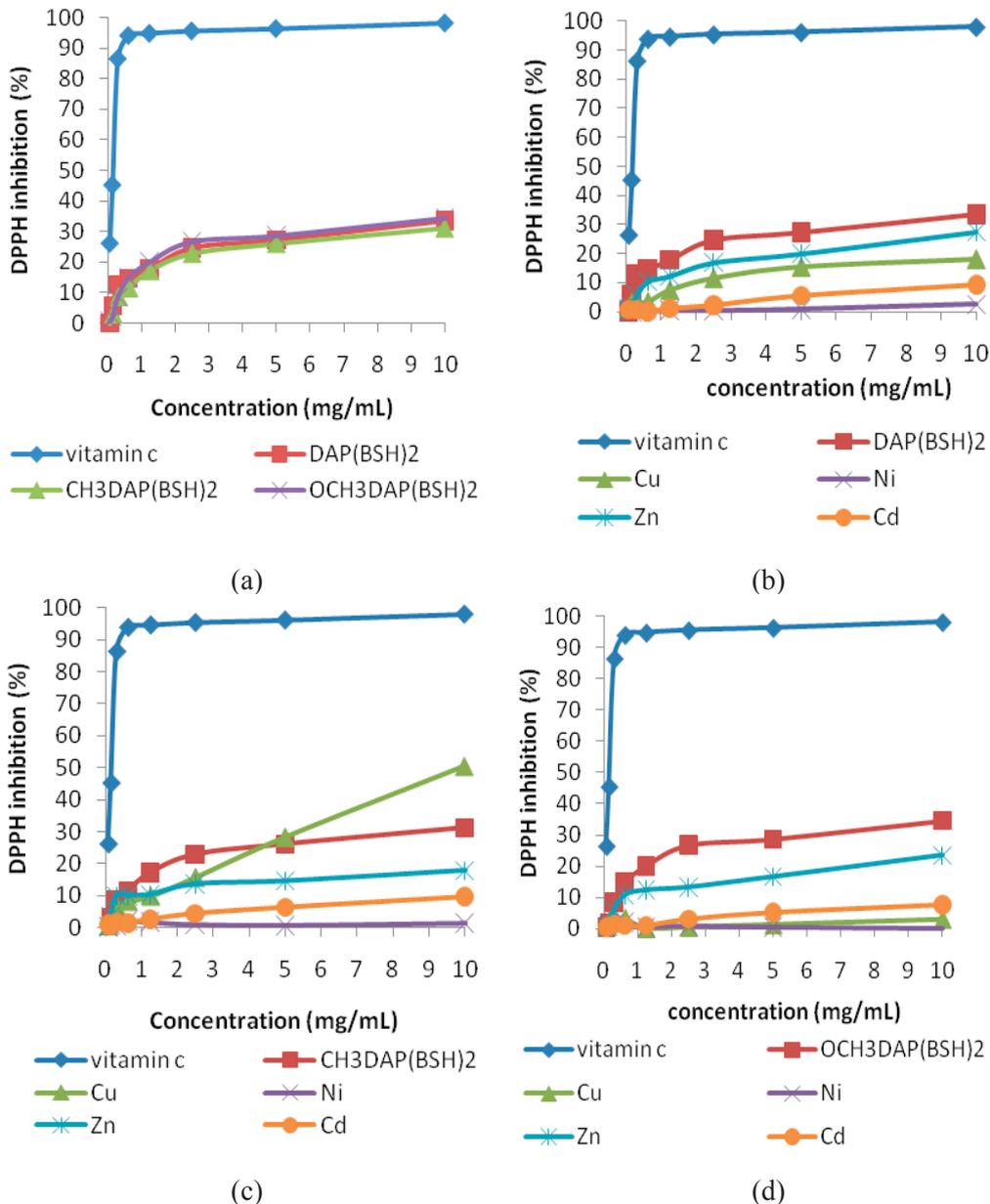


Figure 2 Percentage of DPPH Inhibition for ligands (a) and their complexes (b, c and d)

The results showed that all compounds exhibited marked DPPH free radical scavenging activity in a concentration-dependent manner, but was found to have very low activity to suppress DPPH radicals as ascorbic acid does.

The scavenging activity of DPPH radical in the variety concentration of DAP(BSH)₂, DAP(CH₃BSH)₂ and DAP(OCH₃BSH)₂ is shown in Figure 2(a), giving 31-35% of inhibition. Less scavenging activity may be due to the absence of hydroxyl group in the structure of DAP(BSH)₂ and their derivatives, which is believed to be potent as the hydrogen donor in the scavenging of DPPH radical process. This result is supported by the findings that phenolic or polyphenol compounds exhibit a wide range of biological effects because of the availability of their phenolic hydrogens and the possibility for stabilization of the resulting phenoxyl radicals formed by hydrogen donation in the scavenging of DPPH radical mechanism, thus giving good result in antioxidant activity (Silva *et al.*, 2000 and Soobrattee *et al.*, 2005). Furthermore, ligands of DAP(BSH)₂, DAP(CH₃BSH)₂ and DAP(OCH₃BSH)₂ also displayed an almost equal antiradical potency, indicating the activity of DPPH radical scavenging was not affected in the presence of methyl or methoxy substituent at C-4 of benzenesulphonohydrazine.

A reversal effect of using metal complexes is clearly shown in Figure 2(b)-(d), signifying the chelating Cu(II), Ni(II), Zn(II) and Cd(II) reduced the activity of the DAP(BSH)₂, DAP(CH₃BSH)₂ and DAP(OCH₃BSH)₂ in scavenging of DPPH radical. Zn(II) complexes of DAP(BSH)₂ and DAP(OCH₃BSH)₂ exhibited a better antioxidant activity among of the complexes. The free radical scavenging activity of CuDAP(CH₃BSH)₂ was greater than the parent ligand but only in the concentration of more than 5.0 mg/mL, whereas CuDAP(OCH₃BSH)₂ gave the least activity among the Cu(II) complexes. Cd(II) and Ni(II) complexes were considered having no antioxidant activity when as the percentage of DPPH scavenging activity presented was lower than 10%.

The poor antioxidant activity of metal complexes from the series of DAP(BSH)₂, DAP(CH₃BSH)₂ and DAP(OCH₃BSH)₂ contradict the finding of Howard and Chenier, 1976. The reversed result could be attributed to the unavailability to donate or receive electron and due to their redox stability, thus reduce the ability to act as DPPH radical scavenger (Belicchi-Ferrari *et al.*, 2010). The different relative scavenging ability of individual compound either from the ligands or their complexes against DPPH radical can be explained by the different mechanisms involved in the radical-oxidant reactions. The complexes may also significantly change the chemistry of the free ligand which can enhance or reduce the activity. However, it is impossible to correlate the antioxidant activity of these compounds to any of their structural features due to the limited data.

Conclusion

The Ni(II), Zn(II) and Cd(II) complexes of 2,6-diacetylpyridine bis(benzenesulphonohydrazide) in the series of DAP(BSH)₂, DAP(CH₃BSH)₂ and DAP(OCH₃BSH)₂ are chelated by dianionic pentadentate Schiff base *via* the two azomethine N atoms, two sulfonyl O and pyridine N atom. The antioxidant test for all the compounds reveals that the scavenging of DPPH radical activity of the parent ligands is reduced when they are chelated with Cu(II), Ni(II), Zn(II) and Cd(II) ions. DPPH radical activity however, is not the only aspect to consider to explain antioxidant ability. Thus, other information is also required such as the ability of other ROS such as hydroxyl (OH•), superoxide (O₂⁻), and nitroxyl (NO•) radicals which are considered sensible should be studied as antioxidant potential in future studies.

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