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Synthesis, characterization and antioxidant activity of Schiff base and its metal complexes with Fe(II), Mn(II), Zn(II), and Ru(II) ions: Catalytic activity of ruthenium(II) complex

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ABSTRACT

The synthesis, spectral, catalytic and antioxidant properties of ethyl-2-(2-hydroxy-3-methoxybenzylideneamino)-6-methyl-4,5,6-tetrahydrobenzo[b]thiophene-3-carboxylate (L) substituted iron(II), manganese(II), zinc(II), and ruthenium(II)-arene chlorides are described for the first time. The ligand and its metal complexes were characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, and spectral (^{1}H NMR, ^{13}C NMR, FT-IR, UV-Vis and Mass) techniques. The FT-IR spectra showed that the ligand can act as bidentate or tridentate. Magnetic moments and electronic spectral studies revealed an octahedral geometry for all the complexes obtained. The thermal behavior of the complexes showed that the water molecules were separated in the first step followed immediately by decomposition of the anions and ligand molecules in the subsequent steps. Ru(II) complex was used as catalysts for the transfer hydrogenation of ketones. At the same time, the effect of various bases such as NaOH, KOH, KOBu^t and NaOAc as organic base were investigated in the transfer hydrogenation of ketones by 2-propanol as the hydrogen source. The complexes and ligand were tested *in vitro* for their antioxidant activity. The experimental results showed that Ru(II) complex had more potent antioxidant activities than Zn(II), Fe(II), Mn(II) complexes and parent ligand.

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1. Introduction

In several decades, the studies of Schiff bases have been made to synthesize Schiff bases and their complexes to apply these compounds in the different fields of study [1-6]. So, the metal complexes of Schiff bases have been attracted attention of bioinorganic researches due to their antimicrobial, antibacterial, antifungal, antiviral, anti-mycobacterial, anti-inflammatory, analgesic, anti-tubercular and antioxidant activities [7-9].

Zinc ion is essential for many biological processes such as enzymatic reactions in organisms [10]. The half-sandwich (η^6-arene)Ru complexes are of continuing interest due to their high tolerance towards a variety of functional groups and special reactivity [11].

The searching for new molecules with antioxidant properties is a very active domain of research, since they can protect the human body from free radicals and retard the progress of many chronic diseases, such as vascular diseases, some forms of cancer and oxidative stress responsible for DNA, protein and membrane damage [12]. The radical scavenging activity (RSA) using α,α-diphenyl-β-picrylhydrazyl (DPPH) radical and the reducing power are two established in vitro methods employed for the evaluation of antioxidant activity.

Areneruthenium(II) complexes containing different ligands such as Schiff bases, aryl azo, pincer, carbene and tri-podal are known in the literature [13-15]. Complex formation studies of ruthenium with azo/azoimine ligands and their usage at transfer hydrogenation reaction, metal carbon bond formation and catalytic transformations have been ongoing [16]. Transfer hydrogenation is one of the most important methods for reduction of ketones and aldehydes; due to it is a valuable and atom efficient reaction, more cost effective and simpler experimental procedure [17]. It is a useful method for the reduction of carbonyl compounds to their corresponding alcohols [18,19].

The preparation of a new ligand was perhaps the most important step in the development of metal complexes which show unique properties and novel reactivity. In this study, we prepared the ethyl-2-(2-hydroxy-3-methoxybenzylideneamino)-6-methyl-4, 5, 6-tetrahydrobenzo[b]thiophene-3-carboxylate (L) and its Fe(II), Mn(II), Zn(II), and Ru(II) complexes and characterized by the spectroscopic and analytical methods.

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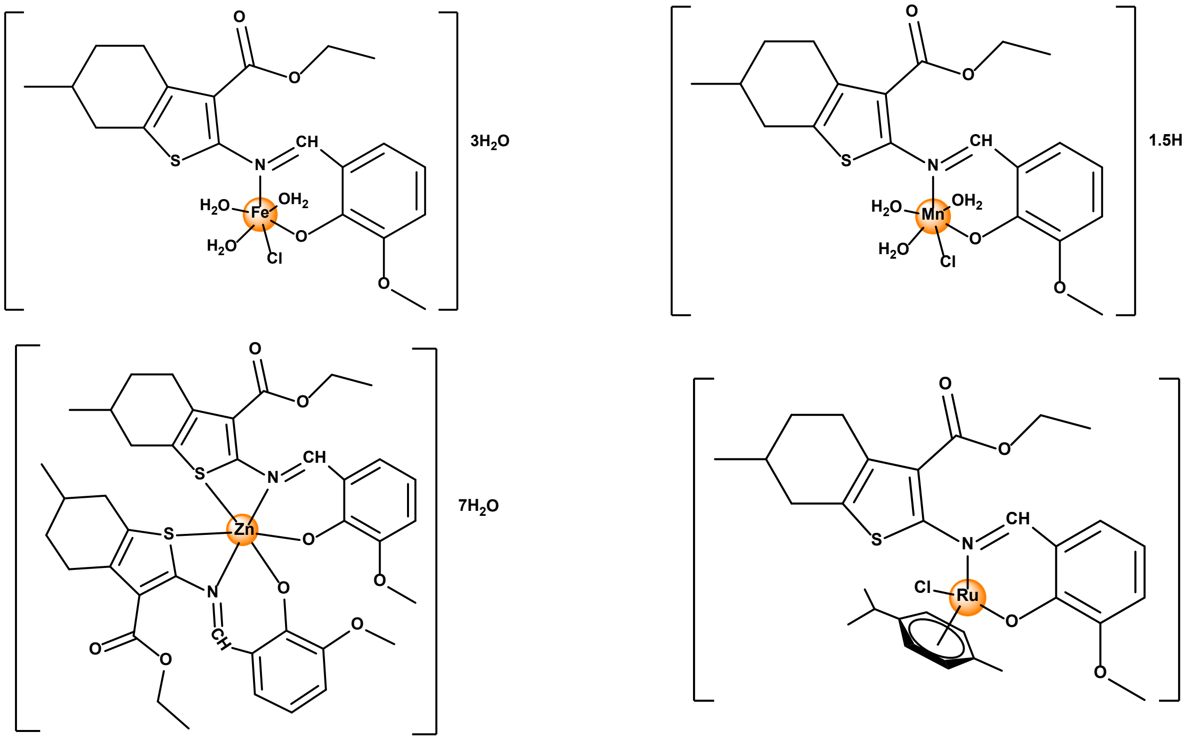


Scheme 1

The antioxidant activity of the ligand and its comp-lexes were determined by DPPH free radical scavenging, ABTS (2,2'-azino-*bis*(3-ethylbenzthiazoline-6-sulfonic acid)) cation radical scavenging, FRAP (Ferric ion reducing power) and CUPRAC (Cupric ion reducing power) assays, and these were applied to determine the antioxidant activity of complexes by *in vitro* methods. Furthermore, the catalytic efficiency of the complex was investigated for the transfer hydrogenation of acetophenones containing different electronic effect to the corresponding secondary alcohols under optimized conditions of base and catalyst loading.

2. Experimental

Solvent and chemicals were obtained from commercial sources and used as such without further purification. Elemental analyses were carried out on a Leco CHNS-O model 932 elemental analyzer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker GmbH DPX-400 MHz FT spectrometer. FT-IR spectra were recorded using Perkin Elmer Precisely Spectrum One spectrometer on KBr discs in the wavenumber range of 4000-400 cm^{-1}. Electronic spectral studies were conducted on a Shimadzu model UV-1800 Spectrophotometer in the wavelength 1100-200 nm. Magnetic susceptibility measurements were performed using the standard Gouy tube technique using Hg[Co(SCN)$_4$] as a calibrate. Thermal analyses (TGA and DTA) were carried out in nitrogen atmosphere with a heating rate of 10 °C/min using Shimadzu DTG-60AH (Shimadzu DSC 60A) thermal analyzers. The molar conductance of solid complexes in DMF was measured using Siemens WPA CM 35 conduct meter. LC/MS-API-ES mass spectra were recorded using an AGILENT model 1100 MSD mass spectrophotometer.

2.1. Synthesis of ligand

2-Hydroxy-3-methoxybenzaldehyde (0.001 mmol) was added to the solution of ethyl 2-amino-6-methyl-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate (0.001 mmol) in ethanol (25 mL). The resulting reaction mixture was stirred at room temperature for 2h and a pale yellow solid was obtained. The solid compound was filtered, washed, and recrystallized from the mixed solvent of chloroform and ethanol (1:3, *v*:*v*).

Ethyl-2-((2-hydroxy-3-methoxybenzylidene)amino)-6-methyl-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate (**HL**): Color: Pale yellow. Yield: 78%. M.p.: 148-150 °C. ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm): 11.10 (s, 1H, Ar-OH), 8.00 (s, 1H, CH=N), 7.00-7.30 (m, 3H, Ar-CH), 4.30 (m, 2H, OCH_2CH_3), 2.92-2.37 (m, 7H, cyclohexyl-CH_2), 0.99-1.88 (m, 9H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6, δ, ppm): 14.10, 21.70, 56.10 (3CH_3), 20.90, 28.90, 32.10, 60.90 (4CH_2), 30.10 (CH), 124.40, 116.60, 115.00, 119.50, 149.00, 150.10 (Ar-H), 138.40, 150.70 (C-S-C), 160.00 (CH=N), 128.00, 136.00 ($C=C_{thiophene}$), 159.90 (C=O). FT-IR (KBr, ν, cm^{-1}):3331, 3316 (OH), 3110 (Ar-CH), 2906 (Aliph.-CH), 1699 (C=O), 1653 (CH=N), 1575 (Ar-C=C), 1390 (C-O), 778 (C-S-C). Anal. calcd. for $C_{20}H_{23}NSO_4$: C, 64.32; H, 6.21; N, 3.75; S, 8.58. Found: C, 64.40; H, 6.20; N, 3.70; S, 8.57%. MS (ESI+, *m/z* (%)): 374.10 [L+H]$^+$.

2.2. Synthesis of Fe(II), Mn(II), Zn(II), and Ru(II) complexes

Fe(II), Mn(II) and Zn(II) complexes were obtained according to a general procedure: The metal salts (1.00 mmol, 0.14 g for $FeCl_2·H_2O$; 0.19 g for $MnCl_2·4H_2O$; 0.17 g for $ZnCl_2·2H_2O$) were dissolved in ethanol and stirred under reflux for 10 min. Followed by the addition of the Schiff base (0.80 g, 2.33 mmol for Fe(II) and Mn(II) complex; and 1.60 g, 4.66 mmol for Zn(II) complex) in ethanol and reaction mixture stirred upon heating for 24 h. The obtained precipitates were filtered, washed with ether and dried in air (Scheme 1).

A solution of ligand (0.37 g, 1.00 mmol) and [$RuCl_2$(η^6-*p*-cymene)]$_2$ (0.31 g, 0.50 mmol) in 10 mL toluene were heated under reflux for 5 h. Upon cooling to room temperature, orange crystals of complex were obtained. The crystals were filtered off, washed with diethyl ether (20 mL) and dried under vacuum. Analytical and spectroscopic results of the Fe(II), Mn(II), Zn(II), and Ru(II) complexes are given below:

$[FeLCl(H_2O)_3]\cdot 3H_2O$: Color: Brownish black. Yield: 70%. M.p.: 265-268 °C. FT-IR (KBr, ν, cm^{-1}): 3300 (OH), 3175, 3062 (Ar-CH), 2948, 2920 (Alip.-CH), 1700 (C=O), 1660 (CH=N), 1596, 1567 (Ar-C=C), 1378 (C-O), 777 (C-S-C), 550 (Fe-O), 467 (Fe-N). Anal. calcd. for $C_{20}H_{34}NSO_{10}FeCl$: C, 42.01; H, 5.99; N, 2.45; S, 5.61. Found: C, 41.95; H, 6.13; N, 2.47; S, 5.60%. MS (ESI+, *m/z*(%)): 573.30 (calcd.), 573.40 (found) $[M+2H]^{2+}$. Λ_m ($\Omega^{-1}cm^2mol^{-1}$): 14. μ_{eff} (B.M.): 5.23.

$[ZnL_2]\cdot 7H_2O$: Color: Brown. Yield: 73%. M.p.: 256-259 °C. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.20 (s, 1H, CH=N), 7.10-7.35 (m, 3H, Ar-CH), 4.33 (m, 2H, OCH_2CH_3), 2.90-2.30 (m, 7H, cyclohexyl-CH_2), 0.99-1.80 (m, 9H, CH_3). FT-IR (KBr, ν, cm^{-1}): 3550-3300 (OH), 3153 (Ar-CH), 2949 (Alip.-CH), 1700 (C=O), 1673 (CH=N), 1590, 1578 (Ar-C=C), 1379 (C-O), 753 (C-S-C), 549, 534 (Zn-O), 494, 472 (Zn-N), 435 (Zn-S). Anal. calcd. for $C_{40}H_{58}N_2S_2O_{15}Zn$: C; 51.31, H; 6.24, N; 2.99, S; 6.85. Found: C; 51.24, H; 6.27, N; 3.00, S; 6.80%. MS (ESI+, *m/z* (%)):936.37 (calcd.), 936.15 (found) $[M+H]^+$. Λ_m ($\Omega^{-1}cm^2mol^{-1}$): 15.30. μ_{eff} (B.M.): Dia.

$[MnLCl(H_2O)_3]\cdot 1.5H_2O$: Color: Brown. Yield: 73%. M.p.: 273-276 °C. FT-IR (KBr, ν, cm^{-1}): $3400_{(broad)}$ (OH), 3159 (Ar-CH), 2937 (Alip.-CH), 1698 (C=O), 1630 (CH=N), 1600 (Ar-C=C), 1365 (C-O), 779 (C-S-C), 554 (Mn-O), 476 (Mn-N). Anal. calcd. for $C_{20}H_{28}NSO_7MnCl\cdot 1.5H_2O$: C; 44.17, H; 5.75, N; 2.58, S; 5.89. Found: C; 44.12, H; 5.69, N; 2.54, S; 5.86%. MS (ESI+, *m/z* (%)):544.39 (calcd.), 544.50 (found) $[M+H]^+$. Λ_m ($\Omega^{-1}cm^2mol^{-1}$): 16.40. μ_{eff} (B.M.): 5.40.

[RuLCl(p-cymene)]: Color: Orange. Yield: 82%. M.p.: 235-239°C. ^1H NMR (400 MHz, DMSO-d_6, δ, ppm): 8.60 (s, 1H, CH=N), 7.30-7.70 (m, 3H, Ar-H), 0.97-1.93 (m, 9H, CH_3), 2.32-2.98 (m, 7H, CH_2), 3.90 (m, 2H, CH_2CH_3), 5.48, 5.38 (d, 4H, CH_3-C_6H_4-$CH(CH_3)_2$ of η^6-*p*-cymene), 3.83 (m, 1H, CH_3-C_6H_4-$CH(CH_3)_2$ of η^6-*p*-cymene), 2.16 (s, 3H, CH_3-C_6H_4-$CH(CH_3)_2$ of η^6-*p*-cymene), 0.91 (6H, d, CH_3-C_6H_4-$CH(CH_3)_2$ of η^6-*p*-cymene). FT-IR (KBr, ν, cm^{-1}): 3342, 3307 (OH), 3051 (Ar-CH), 2929 (CH), 1697 (C=O), 1600 (CH=N), 1571 (Ar-C=C), 1386 (C-O), 1469, 1325, 1130, 876, 751 (Ru-Cl), 779 (C-S-C), 501 (Ru-O), 575 (Ru-N). Anal. calcd. for $C_{30}H_{36}NSO_4ClRu$: C, 56.02; H, 5.64; N, 2.18; S, 4.98. Found: C, 56.00; H, 5.60; N, 2.20; S, 5.00%. MS (ESI+, *m/z*(%)):641.11 (calcd.), 641.00 (found) $[M-2H]^{2-}$.

2.3. General procedure for the transfer hydrogenation of ketones

The catalytic hydrogen transfer reactions were carried out in a closed Schlenk flask under argon atmosphere. A mixture of the required ketone (2 mmol), catalyst [RuLCl(*p*-cymene)] complex (0.01 mmol) and KOH (8 mmol) was heated to reflux in 5 mL of *i*-PrOH for 12 h. Then, the solvent was removed under vacuum, and the residue was extracted with ethyl acetate:hexane (1:5, *v*:*v*), filtered through a pad of silica gel with copious washings, concentrated and purified by flash chromatography on silica gel. The product distribution was determined by ^1H NMR spectroscopy, GC and GC-MS techniques.

2.4. Antioxidant properties

2.4.1. DPPH scavenging activity

The 2,2-diphenyl-1-picrylhydrazyl (DPPH) assay was evaluated to determine the free radical scavenging activities of samples [20]. For this aim, different concentrations (10-30 μg/mL) of samples and standard antioxidants (BHA, BHT and ascorbic acid) were prepared and diluted to 3 mL with ethanol. Then, 1 mL of ethanolic DPPH solution (0.1 mM) was added to the samples. Those samples were vortexed and incubated in the dark at 30 °C for 30 min. The absorbance was measured at 517 nm against blank samples. The percentages of DPPH free radicals' consumption of different concentrations of samples and standards were measured by using the Equation (1).

$$\text{Radical scavenging capability (\%)} = \left(1-\frac{A_{Sample}}{A_{Control}}\right)x100 \tag{1}$$

2.4.2. ABTS•+ scavenging activity

Radical scavenging activities of the prepared complexes were evaluated according to the ABTS method [21]. First of all, ABTS•+ cation radical was produced by reacting ABTS (2 mM) in H_2O and potassium persulphate (2.45 mM) at room temperature for 12 h. The ABTS•+ solution was diluted with phosphate buffer (0.1 M, pH = 7.4) to achieve an absorbance of 0.750±0.025 at 734 nm. Then, 1 mL of ABTS•+ solution was added to 3 mL ethanol at different concentrations (10-30 μg/mL) of samples and standard antioxidants (BHA, BHT and ascorbic acid). Those samples were vortexed and incubated in the dark for 30 min. After 30 min, the absorbance at 734 nm was measured for each concentration relative to a blank.

2.4.3. Ferric reducing antioxidant power (FRAP)

The reducing powers of the prepared complexes was determined by the FRAP method used by Bursal and Gulcin [21]. According to this method, the reduction of Fe^{3+} to Fe^{2+} was determined by measuring the absorbance of Perl's Prussian blue complex. For this aim, different concentrations (10-30 μg/mL) of samples and standard antioxidants (BHA, BHT and ascorbic acid) in distilled water (0.75 mL) were mixed with 1 mL of sodium phosphate buffer (0.2 M, pH = 6.6) and 1 mL (1%) of potassium ferricyanide $[K_3Fe(CN)_6]$. The mixture was incubated at 50 °C for 20 min. Then, the reaction mixture was acidified with 1 mL of trichloroacetic acid (10%). Finally, 0.25 mL of iron(III) chloride (0.1%) was added to that solution. The absorbance of the mixture was measured at 700 nm. A decrease in absorbance indicated increased ferric reducing antioxidant power.

2.4.4. Cupric reducing antioxidant power (CUPRAC)

The cupric ion (Cu^{2+}) reducing powers of complexes were determined by the CUPRAC method proposed by Apak *et al.* [22]. Briefly, 1 mL of 10 mM copper(II) chloride solution, 1 mL of 7.5 mM ethanolic neocuproine solution and 1 mL of 1.0 M ammonium acetate buffer solution were added to a test tube and mixed with 0.25 mL of different concentrations (10-30 μg/mL) of samples. The total volume was adjusted to 4.1 mL with distilled water. The tubes were kept at room temperature. After 30 min of incubation, the absorbance was measured at 450 nm against a blank. Increased absorbance indicates increased Cu^{2+}-Cu^{1+} reduction.

3. Results and discussion

3.1. IR spectra and ^1H NMR spectrum

The IR spectra of the ligand and metal complexes were carried out in the range 4000-400 cm^{-1}. The IR spectrum of the ligand showed a broad band at 3331 to 3316 cm^{-1} which can be attributed to phenolic-OH group. This band was disappeared in all complexes spectra, owing to deprotonation of phenolic-OH group. The involvement of deprotonated phenolic moiety in complexes was confirmed by the shift of ν(C-O), stretching band observed at 1390 cm^{-1} in the ligand, to a lower frequency to the extent of 4-25 cm^{-1}. The shift of ν(C-O) band at 1386-1365 cm^{-1} to a lower frequency suggested the weakening of ν(C-O) [23] and formation of stronger M-O bond. No shift was observed in the asymmetric and symmetric stretching vibrations of ester carbonyl, this supported the non-involvement of carboxylate groups in metal coordination. In the spectra of ligand, the strong band was observed at 1653 cm^{-1} that could be assigned to ν(CH=N) [23,24]. These frequencies, which are shifted towards a higher or lower wave number by 20-53 cm^{-1} in the spectra of metal complexes, indicate coordination of nitrogen of the azomethine group of the central metal atom in complexes [25]. This assumption was confirmed by the presence of ν(M-N) and ν(M-O) bands at 575-467 and 554-501 cm^{-1} in the far IR region of the complexes [24-27]. Thiophene ν(C-S-C) stretching was observed at 778 cm^{-1} in the ligand. In Zn(II) complex, that band confirming the involvement of the thiophene sulfur in complex formation appeared at lower frequencies in 753 cm^{-1} region [28,29]. Also, the IR bands near 435 cm^{-1} was ascribed to ν(M-S). This presented a good evidence for the participation of sulfur atom in bond formation [30]. The presence of coordinated water in the complexes was indicated by a broad trough band in the region 3550-3300 cm^{-1}and two weaker bands in the region 868 and 822 cm^{-1} due to ν(OH) rocking and wagging mode of vibrations, respectively [31]. The IR spectrum of Ru(II)-arene complex, though not showing the Ru-N vibration which lie below 500 cm^{-1}, was in accordance with this structure since a red shift was observed for the ligand's CH=N bands associated with metal coordination [32].

From the infrared spectra of Fe(II) and Mn(II) complexes, it was apparent that, the chelation of the divalent metal ions to the ligand occurred from the ligand through the oxygen atoms of the phenol moiety and the nitrogen atom of the azomethine groups in the ligand. The chlorine atoms and coordinated water molecules connected to the other coordination sites to complete the geometry of the central metal ion.

The ^{1}H NMR spectrum of ligand was recorded in dimethylsulfoxide (DMSO-d_6) solution using tetramethylsilane (TMS) as internal standard. The spectrum of the complexes is examined in comparison with of the ligand. The ^{1}H NMR spectrum of the diamagnetic Zn(II) and Ru(II) complexes show almost the same values as that of the ligand. Upon examinations, it was found that the phenolic-OH signal, appeared in the spectrum of ligand at δ 11.10 ppm is completely disappeared in the spectra of its Zn(II) and Ru(II) complexes indicating that the OH proton is removed by the complexation with Zn(II) and Ru(II) ions. Also the signal observed at δ 4.30 ppm with an integration corresponding to protons in case of Zn(II) complex is assigned to seven water molecules. In the NMR spectrum of Ru(II) complex, the signals were observed in δ 8.60 ppm supporting the coordination of imino nitrogen atom to Ru(II) complex.

3.2. Electronic spectra, magnetic moment and molar conductivity

The UV-Vis spectra of the ligand and its metal(II) complexes were recorded in DMF solution in the wavelength range 200-1100 nm. The electronic spectra of the ligand exhibited two bands in the region 274 and 373 nm. These might be assigned due to the $n\rightarrow\pi^*$ and $\pi\rightarrow\pi^*$. A careful comparison of these bands with the electronic spectra of complexes showed that there was an increase in intensity and a decrease in frequency due to extended conjugation in the ligand after complexation. Further, weak bands appearing at 319 and 422 nm were attributed to the metal-to-ligand charge transfer transitions (MLCT), transitions arising possibly due to transfer of electron from the filled *d*-orbital of coordinated oxygen to the vacant *d*-orbital of metal [33,34].

Magnetic susceptibility measurements of the complexes were made at room temperature, which indicate that the Mn(II) and Fe(II) complexes were paramagnetic, corresponding to 2+ oxidation state of manganese and iron in those complexes. At room temperature magnetic moment of the Mn(II) complex lied at 5.40 B.M. corresponding to five unpaired electrons. Electronic spectra of Mn(II) complex exhibited weak intensity absorption bands at 218-382 and 489 nm. These bands might be assigned to the transitions: $^4A_{1g}\rightarrow{}^6A_{1g}$, $^4T_{1g}(G)\rightarrow{}^6A_{1g}$, $^4T_{1g}(D)\rightarrow{}^6A_{1g}$, respectively [35,36]. The electronic spectrum of the Fe(II) complex displayed two absorption bands at 319 and 620 nm which were assigned to $^5T_{2g}\rightarrow{}^5E_g$ transitions [37]. Also, the band at 429 nm is assigned to L → M charge transfer [38]. The Fe(II) complex had a magnetic moment value of 5.23 B.M. which was consistent with high spin octahedral geometry [39,40]. The Zn(II) complex was diamagnetic and according to the empirical formula, an octahedral geometry was proposed for this complex. Due to the complete d^{10} electronic configuration, *d-d* transition band was not observed [41]. H_2O molecules in the complexes have been suggested by thermal analysis study.

The molar conductance values of the Fe(II), Mn(II) and Zn(II) complexes in DMF solution were found in the range Λ_M = 14.00-16.40 $\Omega^{-1}cm^2mol^{-1}$, indicating that the non-electrolytic nature of the complexes in the DMF solution [40].

3.3. Thermogravimetric analysis (TGA)

Thermal analyses were carried out in the temperature range from 25 to 800 °C in nitrogen atmosphere by Shimadzu DTG-60 AH thermal analyzer. The experimental conditions were platinum crucible with 1 mg of sample and heating rate of 10 °C/min. Thermograms of the Fe(II), Mn(II) and Zn(II) complexes showed three steps of decomposition within the temperature range 50-600 °C. The first and second steps occurred within the temperature range 50-300 °C and it involved the loss of H_2O, Cl and $COOC_2H_5$ molecules with mass losses of 38.28% (calculated mass loss 37.90%), 21.04% (calculated mass loss 21.49%) and 13.57% (calculated mass loss 13.47%) for Fe(II), Mn(II), and Zn(II) complexes, respectively. The loss of the ligand occurred within the temperature range 300-600 °C. The total weight loss amounts were 53.33% (calculated mass loss 52.40%), 56.57% (calculated mass loss 56.75%) and 75.95% (calculated mass loss 76.12%) for Fe(II), Mn(II), and Zn(II) complexes, respectively. The sequences for thermal decomposition of the complexes $[FeLCl(H_2O)_3]\cdot 3H_2O$, $[MnLCl(H_2O)_3]\cdot 1.5H_2O$ and $[ZnL_2]\cdot 7H_2O$ are given in Table 1. Thermal behavior of the complexes is almost the same. Hence, only complexes were discussed in general [42].

3.4. Antioxidant activity of ligand and metal complexes

The antioxidant properties of hydrazones and their metal complexes have attracted a lot of interests and have been investigated mainly in the *in vitro* systems [43,44]. The antioxidant activities of ethyl 2-amino-6-methyl-4,5,6,7-tetrahydrobenzo[b]thiophene-3-carboxylate (L) and its metal complexes were evaluated by four *in vitro* methods; DPPH free radical scavenging, ABTS cation radical scavenging, FRAP and CUPRAC assays. We used standard antioxidants (BHA, BHT and ascorbic acid) in order to compare the results and to establish some structure antioxidant-activity relationships for each method.

The parent ligand of this study has aromatic rings with a phenolic structure. Phenolic compounds can interrupt chain oxidation reactions by donation of a hydrogen atom or chelating metals. Chemical structure of aromatic ring and the number of hydroxyl groups are important associated factors on antioxidant abilities [45].

The ABTS assay is widely used to evaluate the radical scavenging activity of antioxidant compounds. According to the ABTS assay, antioxidant capacity of a compound is based on measuring the reduction of $ABTS^{\bullet +}$ cation radicals [26,46].

Table 1. Proposed decomposition steps and the respective mass losses of the ligand and its complexes.

Compounds	Temperature (°C)	Loss in weight, %Calculated (Found)	Dec. products
[HL] ($C_{20}H_{23}NSO_4$)	90-261	12.33 (12.86)	C_2H_5OH
$C_{18}H_{17}NSO_3$	261-476	87.66 (87.14)	$C_{18}H_{17}NSO_3$
$[FeLCl(H_2O)_3]\cdot 3H_2O$ ($C_{20}H_{34}NSO_{10}FeCl$)	50-150	9.43 (9.42)	$3H_2O$
$C_{20}H_{28}NSO_7FeCl$	150-300	28.47 (28.86)	$3H_2O$, Cl, $COOC_2H_5$
$C_{17}H_{17}NSO_2Fe$	300-600	49.61 (49.56)	$C_{17}H_{17}NSO_2$
Fe	-	-	-
$[MnLCl(H_2O)_3]\cdot 1.5H_2O$ ($C_{20}H_{28}NSO_7MnCl.1.5H_2O$)	50-100	4.96 (5.00)	$1.5H_2O$
$C_{20}H_{28}NSO_7MnCl$	100-200	16.53 (16.04)	$3H_2O$, Cl
$C_{20}H_{22}NSO_4Mn$	250-500	56.75 (56.57)	$C_{20}H_{22}NSO_3$
MnO	-	-	-
$[ZnL_2]\cdot 7H_2O$($C_{40}H_{58}N_2S_2O_{15}Zn$)	50-200	13.47 (13.57)	$7H_2O$
$C_{40}H_{44}N_2S_2O_8Zn$	200-300	39.77 (39.29)	$C_{20}H_{22}NSO_4$
$C_{20}H_{22}NSO_4Zn$	300-600	38.06 (38.17)	$C_{20}H_{22}NO_4$
ZnS	-	-	-

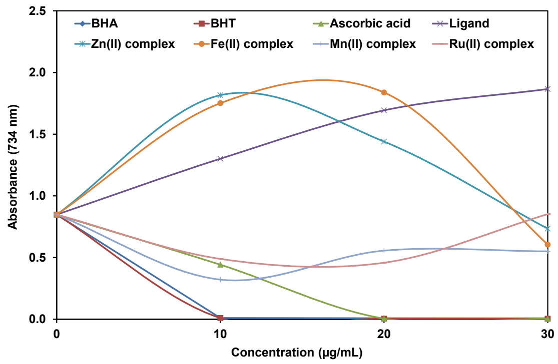


Figure 1. ABTS radical scavenging activities of complexes and standard antioxidants (Ascorbic acid, BHT and BHA).

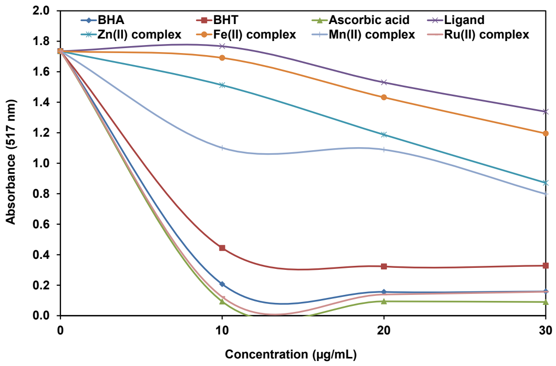


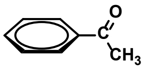
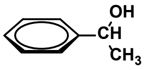
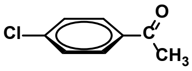
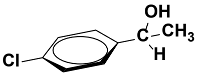
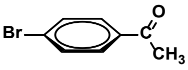
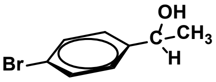
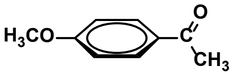
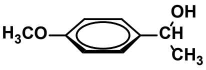
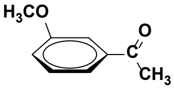
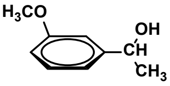
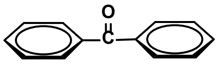
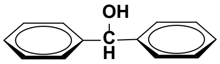
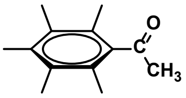
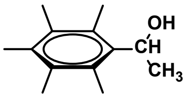
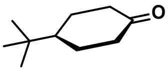
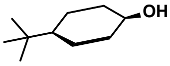
Figure 2. DPPH free radical scavenging activities of complexes and standard antioxidants (Ascorbic acid, BHT and BHA).

It was observed that complexes of ligand had low $ABTS^{\bullet +}$ radical scavenging activity but parent ligand did not show significant $ABTS^{\bullet +}$ radical scavenging activity (Figure 1). The results are dependent on the molecule's structure and single electron transfer potential.

DPPH assay is the most common method to evaluate the antioxidant properties of compounds or extracts [47]. DPPH free radical scavenging effect of ligand and its complexes enhanced with their growing concentration, and Ru(II) complex exhibited the highest ability to scavenge DPPH•. Scavenging activities of ligand and its Mn(II), Fe(II), Zn(II) complexes were considered medium levels compared to BHA, BHT and vitamin C, under the same conditions at the concentration of 10-30 μg/mL (Figure 2). According to the result of this study, the free radical inhibition of standard antioxidants, ligand and its metal complexes were decreased in the following order: ascorbic acid (94.8%) > Ru(II) complex (94.4%) > BHA (90.8%) > BHT (81.1%) >Mn(II) complex (52.2%) > Zn(II) complex (49.8%) > Fe(II) complex (31.1%) > L (22.9%), in presence of same concentration (30 μg/mL) of test sample.

Reducing powers of complexes and standard antioxidants (Ascorbic acid, BHT and BHA) were evaluated by FRAP assay. Antioxidant compounds cause the reduction of ferric ions (Fe^{3+}) to ferrous ions (Fe^{2+}), because of their reductive capabilities. Ferric reducing antioxidant powers of a com-pound can be measured by this transformation level [23,46]. According to the result of this study, the reducing power of standard antioxidants, ligand and its metal complexes were decreased in the following order: BHA > BHT >Ascorbic acid >Ru(II) complex > Zn(II) complex > Ligand > Fe(II) complex >Mn(II) complex, in presence of same concentration (30 μg/mL) of test sample. Figure 3 demonstrated the reducing powers of standard antioxidants, ligand and its metal complexes. A positive correlation was also found between the antioxidant activity and the concentration of samples. Ferric reducing powers of samples were increased by increasing concentration.

Table 2. Catalytic activity for transfer hydrogenation of acetophenone catalyzed by Ru(II) complexes with different ba

Entry	Ketone	Alcohol	Base	Conversion (%)
1			KOH	98
2			NaOH	60
3			K_2CO_3	58
4			KOBu^t	42
5			NaOAc	41
6			Cs_2CO_3	27
7			KOH	100
8			NaOH	64
9			K_2CO_3	18
10			KOBu^t	43
11			NaOAc	58
12			Cs_2CO_3	61
13			KOH	100
14			NaOH	61
15			K_2CO_3	48
16			KOBu^t	38
17			NaOAc	51
18			Cs_2CO_3	29
19			KOH	81
20			NaOH	24
21			K_2CO_3	35
22			KOBu^t	21
23			NaOAc	28
24			Cs_2CO_3	37
25			KOH	100
26			NaOH	68
27			K_2CO_3	54
28			KOBu^t	50
29			NaOAc	58
30			Cs_2CO_3	60
31			KOH	97
32			NaOH	74
33			K_2CO_3	69
34			KOBu^t	57
35			NaOAc	39
36			Cs_2CO_3	49
37			KOH	97
38			NaOH	71
39			K_2CO_3	65
40			KOBu^t	66
41			NaOAc	54
42			Cs_2CO_3	61
43			KOH	74
44			NaOH	40
45			K_2CO_3	35
46			KOBu^t	29
47			NaOAc	32
48			Cs_2CO_3	27

Reaction conditions: Reactions were carried out at 80 °C using ketone (2 mmol), catalyst (1mol %), base (8 mmol), *i*-PrOH (5 mL) for 12 h.

In the present work, we used the CUPRAC method to determine the reducing power of Mn(II) and Ru(II) complexes and standard antioxidants (Ascorbic acid, BHT and BHA). Antioxidant compounds cause the reduction of cupric ions (Cu^{2+}) to cuprous ions (Cu^{+}), because of their reductive capabilities [27]. It was found that the cupric reducing power of Ru(II) complex was at a high level, similar to the levels of standard antioxidants. Figure 4 demonstrated the cupric reducing powers of standard antioxidants ligand and its metal complexes.

3.5. Catalytic transfer hydrogenation of ketones

Catalytic studies with Ru(II) was performed for the transfer hydrogenation (TH) of acetophenone to give phenyl ethanol in the presence of base by 2-propanol as a hydrogen source (Table 2). Due to the promoted applications of half-sandwich ruthenium compounds in transfer hydrogenation catalysis, we also investigated the catalytic activity of the complex Ru(II) toward reduction of carbonyl group of ketones. Acetophenone was chosen as a model substrate to explore the catalytic performance of the complexes. Following the selection of complex test reactions were performed with different base types, amounts and substrate/catalyst ratios to optimize and find out the best catalytic reaction conditions. For this purpose, first of all the influence of base type was investigated by using bases such as NaOH, KOH, NaOAc, K_2CO_3, $CsCO_3$ and KOBu^t. Among the different bases used for our studies, the KOH was the best choice of base and the conversion of product could be increased to 100% (Table 2, entries 7, 13, 25).

On the other hand acetophenone and *o*-, *m*- and *p*-substituent acetophenone derivatives were transformed to the corresponding secondary alcohols. Under these conditions *p*-methoxyacetophenone, *p*-bromoacetophenone and *p*-chloroacetophenone react very cleanly and in good yields with 2-propanol (Table 2, entries 1, 7, 13, 19). The presence of electron with drawing (Cl) or electron donating (OCH_3) substituents on acetophenone was a significant effect on the reduction of ketones to their corresponding alcohols. It was observed that the presence of electron releasing -OCH_3 group on them-position of aromatic ring possibly increased the elec-

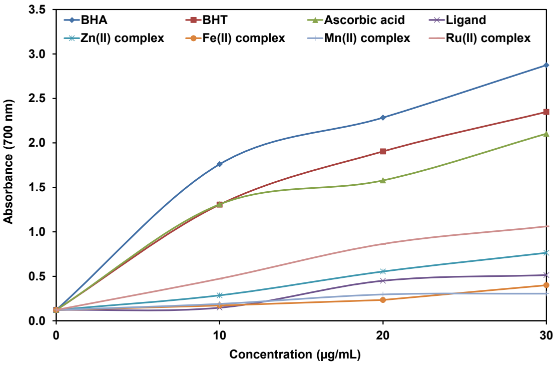


Figure 3. Reducing powers of complexes and standard antioxidants (Ascorbic acid, BHT and BHA) by FRAP assay.

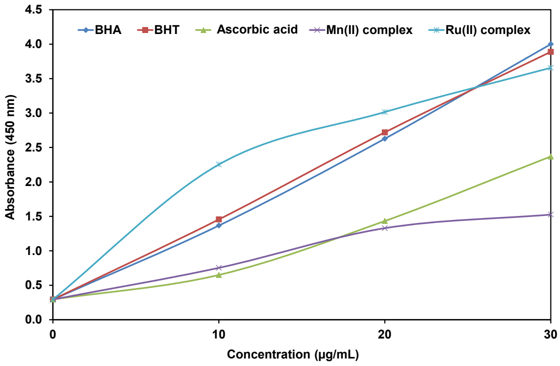


Figure 4. Reducing powers of complexes and standard antioxidants (Ascorbic acid, BHT and BHA) by CUPRAC assay.

tron density on the metal center and hence the rate of transfer hydrogenation increases (Table 2, entries 19,25). No significant changes in the yield observed when the pentamethyl-substituents were located in the *o*-, *m*- and *p*-positions of the acetophenone (Table 2, entry 37). We also tested this reaction on benzophenone plays a significant role in the conversion of ketones to alcohols (Table 2, entry 31). Furthermore, *p*-tertiarymethylcyclohexanone were observed lower yield (Table 2, entry 43, 74%). Substrate with electron-with drawing substituents such as Cl, Br plays a significant role in the conversion of ketones to alcohols (Table 2, entries 7, 13) and catalyze with good conversions of 100%. The introduction of electron-donating substituents to the meta position of the aryl ring of the ketone conversion decreased, however electron-donating substituents to the para position of the aryl ring of the ketone conversion is increasing (Table 2, entries 19, 25) 81 and 100%, respectively [16].

4. Conclusion

Based on chemical and spectral data discussed above, octahedral geometry for Fe(II), Mn(II), Zn(II) and Ru(II) complexes was proposed. The spectral data showed that ligand existed as bidentate or tridentate ligand by bonding to the metal ion through the deprotonated enol/thiol-O/S groups and azomethine nitrogen. The analytical data showed the presence of one metal ion per two ligand molecules and suggested a mononuclear structure for the Zn(II) complexes. The experimental results showed that Ru(II) complex had more potent antioxidant activities than Zn(II), Fe(II), Mn(II) complexes and parent ligand. Ru(II) complex showed good catalytic activity and so the effects of the different groups were also examined. Ru(II) complex was found to convert substituted acetophenone derivatives to the corresponding alcohols at high ratios using potassium hydroxide in isopropyl solvent. Excellent reaction results were obtained in the hydrogenation reactions, offering wide functional group compatibility, varying substrate coverage.

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Disclosure statement DS

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Author contributions: All authors contributed equally to this work.
Ethical approval: All ethical guidelines have been adhered.
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