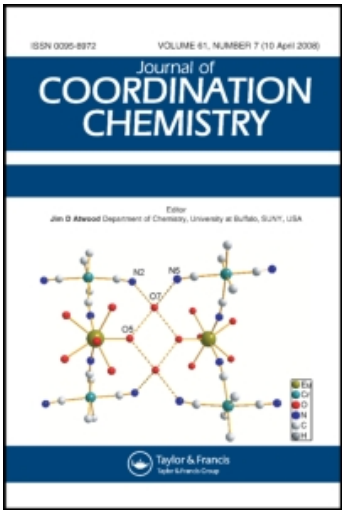

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Synthesis and spectroscopic studies of some halogen-dimethylsulphoxide/tetramethylenesulphoxide-ruthenium(II) and ruthenium(III) complexes with 2-aminobenzimidazole

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Synthesis and spectroscopic studies of some halogen-dimethylsulphoxide/tetramethylenesulphoxide-ruthenium(II) and ruthenium(III) complexes with 2-aminobenzimidazole†

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Synthesis and characterization of seven ruthenium(II) and ruthenium(III) complexes of sulphoxide with 2-aminobenzimidazole are reported. Three different formulations exist; [*cis*-$RuCl_2(SO)_3$(2-ABZ)]; [*trans*-$RuCl_2(SO)_3$)(2-ABZ)]; and [*trans*-$RuCl_4$(SO)(2-ABZ (where SO = dimethylsulphoxide(DMSO)/tetramethylenesulphoxide(TMSO); 2-ABZ = 2-aminobenzimidazole). These complexes are characterized by elemental analysis, conductivity magnetic susceptibility, ^{1}H-NMR, $^{13}C\{^1H\}$-NMR and electronic spectroscopy.

Keywords: Ruthenium; Dimethylsulphoxide; Tetramethylenesulphoxide; Aminobenzimidazole

1. Introduction

Ruthenium complexes, known for their catalytic ability are providing a tool in fighting cancer [1–4]. An extensive study made by Alessio, Sava, Mestroni and group led to the synthesis of NAMI-A; *trans*$[Ru^{III}Cl_4(DMSOIm]^-[ImH]^+$, which entered clinical trials in 2000 and successfully completed it [5]. NAMI-A is not very toxic to primary cancer cells, but is very effective in preventing metastasis. Similarly, the entering of a second ruthenium complex, indazolium [tetrachlorobis(indazole)Ru^{III}], in clinical trials, has given a great thrust to ruthenium based pharmaceutical chemistry [6, 7]. This new complex is quite active against colon carcinomas and their metastasis [8].

Therefore, it is of interest to synthesize biologically active ruthenium sulphoxide complexes coupled with biologically-active heterocyclic ligands like 2-aminobenzimidazole.

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†Dedicated to my teacher and mentor, Dr R.S. Srivastava, Associate Professor, University of Lousiana at Lafayette, USA.

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2. Experimental

$RuCl_3 \cdot 3H_2O$ (E. Merck), 2-aminobenzimidazole (Lancaster, UK) and tetramethylene sulphoxide (Lancaster, UK) were used as received. Analytical grade dimethylsulphoxide (BDH) and routine solvents were used without further purification for synthetic purposes.

Electronic absorption spectra were recorded with Systronics-2201, double beam spectrophotometer equipped with a PC. Conductivity measurements were carried out at 25°C on a Elico CM-180 conductivity bridge with a dipping type cell. FTIR spectra were recorded in KBr pellets on Perkin-Elmer Spectrum RXI. ^{1}H-NMR and $^{13}C\{^1H\}$-NMR spectra were recorded in acetone d_6/DMSO-d_6 on a Bruker DRX-300 spectrometer. Guoy's method was employed for measurement of magnetic susceptibility. Cobalt mercury tetrathiocyanate was used as standard. Diamagnetic correction was made using Pascal's constant.

2.1. *Synthesis of complexes*

2.1.1. Synthesis of *cis*-dichlorotris(dimethylsulphoxide)-2-aminobenzimidazole ruthenium(II)[*cis*-$RuCl_2(DMSO)_3$(2-ABZ)], (1)

(a) The starting complex, *cis*-$RuCl_2(DMSO)_4$, was prepared according to the method reported by Evans *et al.* [9].

(b) Recrystallized *cis*-$RuCl_2(DMSO)_4$ (0.100 g, 0.0002 mol), was dissolved in 10 mL of methanol in a two neck flask and 2-aminobenzimidazole (0.050 g, 0.00037 mol) dissolved in a minimum volume of methanol, was added to, and refluxed for 18 h, under inert atmosphere. The reaction mixture was evaporated and reduced to half by passing a flux of N_2 gas. A dark brown solid precipitated, which was washed with acetone and recrystallized from acetone/methanol (2 : 8), and dried in vacuum. Yield 0.080 g (72%). m.p. > 225. Found: C, 28.02; H, 4.30; N, 7.62; S, 17.52. $C_{13}H_{25}N_3S_3O_3Cl_2$ Ru (M_τ 539) requires C, 28.93; H, 4.67; N, 7.78; S, 17.82. Selected infrared absorptions (KBr, cm^{-1}); ν_{SO} 1099(s); ν_{RuCl} 334(s), 330(sh); ν_{RuS}, 402(m); $\nu_{(CNcyclic)}$, 1595(s); ν_{Ru-N}, 272(s); $\nu_{(NH)}$, 3442(m); 3420(m); Electronic spectra (λ_{max}, nm (ϵ in $M^{-1}cm^{-1}$)) in acetone solution, 366(864); 324(630); 250(1105). Δ_M at 25°C ($\Omega^{-1}cm^2mol^{-1}$); 35 in acetone. ^{1}H-NMR spectra: (δ value in ppm) δ (Ar–H), 7.05–7.82 (4H); δ (N-H), 10.51 (H); δ (NH_2), 8.35 (2H); δ (CH_3), 3.56 (6H); 3.42 (12H). $^{13}C\{^1H\}$-NMR: (δ value in ppm) δ(Ar–C), 116.681δ (S–C),56.281,54.362;δ(C–NH_2),128.68.

2.1.2. Synthesis of *trans*-trichlorotris(dimethylsulphoxide)-2-aminobenzimidazole ruthenium(II)–[*trans*-$RuCl_2(DMSO)_3$(2-ABZ)], (2)

(a) The starting complex *trans*-$RuCl_2(DMSO)_4$ was prepared according to the method reported by Alessio *et al.* [1].

(b) Recrystallized *trans*-$RuCl_2(DMSO)_4$ (0.100 g, 0.0002 mol) was taken into 10 mL of methanol in a two neck flask and 2-aminobenzimidazole (0.055 g, 0.00042 mol) dissolved in minimum volume of methanol, was added and stirred for 6–8 h. The colour changes from deep yellow to red-orange and then brown. The reaction

solution was evaporated under vacuum and a brown red solid precipitated, which was washed several times with acetone and diethyl ether and recrystallized from methanol/acetone. Yield 0.055 g (50%). m.p. > 225. Found: C, 28.06; H, 4.44; N, 7.81; S, 17.48; $C_{13}H_{25}N_3S_3O_3Cl_2$ Ru ($M_\tau = 539$) requires C, 28.90; H, 4.60; N, 7.70; S, 17.80; Selected infrared absorptions (KBr, cm^{-1}); ν_{SO} 1090(s); ν_{Ru-Cl} 332(s), ν_{Ru-S}, 401(m); $\nu_{(CNcyclic)}$, 1598(s); ν_{Ru-N}, 270(m); $\nu_{(NH)}$, 3450 (m), 3422 (m); Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetone, 448(732); 339.5(965); 299(860). Δ_M at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$); 40 in acetone. ^{1}H-NMR spectra: (δ value in ppm) δ (Ar–H), 7.20−7.75 (4H); δ (N–H), 10.50 (H); δ (NH_2), 8.32 (2H); δ (CH_3), 3.46 (12H); 3.58 (6H). $^{13}C\{^1H\}$-NMR: (δ value in ppm) δ (Ar–C), 119.491, δ (S–C), 54.268,52.697;δ (C-NH_2),131.621.

2.1.3. Synthesis of (2-aminobenzimidazolium)*trans*-tetrachloro(dimethylsulphoxide) (2-aminobenzimidazole ruthenate(III), $[2\text{-ABZ}]^+[$*trans*-$RuCl_4$(DMSO-S) (2-ABZ)$]^-$, (3)

(a) The starting complex $[(DMSO)_2H][$*trans*-$Ru(DMSO)_2Cl_4]$ was prepared according to the method reported by Alessio *et al*. [2].

(b) $[(DMSO)_2H][$*trans*-$Ru(DMSO)_2Cl_4]$, (0.100 g, 0.00018 mol) was dissolved in 20 mL of methanol. 2-Aminobenzimidazole (0.055 g, 0.00041 mol) dissolved in a minimum volume (5 mL) of 1 N HCl and 10 mL of methanol was added to the above reaction mixture and refluxed under inert atmosphere for 20 h. Reaction mixture was evaporated to half of its volume. A brown black precipitate was further purified by column chromatography using silica gel (60–120 mesh). The desired product was isolated by eluting the column by a 4 : 1, v/v benzene-acetone mixture. Evaporation of the solvent from the eluate yielded a dark brown solid. Yield 0.256 g (44%). m.p. > 225. Found: C, 32.06; H, 3.45; N, 14.02; S, 5.03; $C_{16}H_{21}N_6SOCl_4$ Ru ($M_\tau = 588$) requires C, 32.66; H, 3.58; N, 14.28; S, 5.44. Selected infrared absorptions (KBr, cm^{-1}); ν_{SO} 1108(s); ν_{RuCl} 338(s); ν_{Ru-S}, 402(m); $\nu_{(CNcyclic)}$, 1596(s); ν_{Ru-N}, 275(m); $\nu_{(NH)}$, 3448 (m); 3428 (m); Electronic spectra (λ_{max}, nm ($\in$ in $M^{-1}\,cm^{-1}$)) in DMSO, 488(680); 429(1020) in H_2O 470(350), 400(1050), 300(860). $\mu_{eff} = 1.86_{\mu B}$. Δ_M at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 80 in DMSO; 65 in acetone; 150 in H_2O.

2.1.4. Synthesis of sodium *trans*-tetrachloro-(dimethylsulphoxide) (2-aminobenzimidazole) ruthenate(III), Na[*trans*-$RuCl_4$(DMSO-S)(2-ABZ)], (4)

(a) The starting complex Na[*trans*-$Ru(DMSO)_2Cl_4$] was prepared by the method reported by Alessio *et al*. [2].

(b) Recrystallized complex Na[*trans*-$RuCl_4(DMSO)_2$], (0.100 g, 0.00024 mol) was dissolved in 20 mL of methanol and 2-aminobenzimidazole (0.068 g, 0.00051 mol) dissolved in minimum volume (5 mL) of 1 N HCl and 10 mL of methanol, was added and refluxed for 12 h in an inert atmosphere. The reaction mixture was concentrated to half of its volume giving a brown precipitate, which was further purified by column chromatography using silica gel (60–120 mesh). The desired product was obtained by eluting the column by 8 : 3, v/v benzene-acetonitrile. Reddish-brown compound was obtained on vacuum evaporation. Yield 0.065 g (58%). m.p. > 225. Found: C, 22.26; H, 2.72; N, 8.54; S, 6.42; $C_9H_{13}N_3SOCl_4$

RuNa ($M_\tau = 477$) requires C, 22.78; H, 2.74; N, 8.86; S; 6.75. Selected infrared absorption (KBr, cm^{-1}), $\nu_{(CNcyclic)}$, 1598(s); ν_{SO} 1098(s); ν_{RuCl} 334(s); ν_{Ru-S}, 400(m); ν_{Ru-N}, 270(m); $\nu_{(NH)}$, 3445 (m); 3420 (m); Electronic spectra (λ_{max}, nm ($\in$ in $M^{-1}\,cm^{-1}$)) in acetone, 476(680); 348(860); 303(755). $\mu_{eff} = 1.87\mu_B$. Δ_M at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 80 in DMSO; 96 in H_2O.

2.1.5. Synthesis of *cis*-dichlorotris(tetramethylenesulphoxide)(2-aminobenzimidazole) ruthenium(II), [*cis*-$RuCl_2(TMSO)_3$(2-ABZ)], (5)

(a) From recrystallized *cis*-$RuCl_2(DMSO)_4$, *cis*-$RuCl_2(TMSO)_4$ was prepared using the alternative procedure proposed by Alessio *et al*. [10], which involves DMSO/TMSO ligand exchange.

(b) Recrystallized *cis*-$RuCl_2(TMSO)_4$, (0.100 g, 0.00017 mol) was dissolved in 20 mL of ethanol with mild stirring. 2-Aminobenzimidazole (0.060 g, 0.00045 mol) was dissolved in minimum ethanol, added to the above solution and refluxed for 15 h. The solution obtained was reduced to half by passing a flux of N_2 over hot liquid. A black brown powder was obtained, which was filtered and recrystallized from acetone/ether, 5 : 1, v/v and dried in vacuum. Yield 0.075 g (70%). m.p. > 225. Found: C, 36.82; H, 5.01; N, 6.42; S, 15.45; $C_{19}H_{31}N_3S_3O_3Cl_2Ru$ ($M_\tau = 617$) requires C, 36.95; H, 5.05; N, 6.80; S, 15.57; Selected infrared absorptions (KBr, cm^{-1}); ν_{SO} 1120(s); ν_{CN} 1594(s); ν_{Ru-Cl} 326(s), 330 (m); ν_{Ru-S}, 398(m); ν_{Ru-N}, 271(s); $\nu_{(NH)}$, 3440 (m); 3425 (m); Electronic spectra (λ_{max}, nm ($\in$ in $M^{-1}\,cm^{-1}$)) in acetone. 361(450); 307(352); 258(8078). Δ_M at 25°c($\Omega^{-1}\,cm^2\,mol^{-1}$); 52 in acetone. ^{1}H-NMR spectra: (δ value in ppm) δ (Ar–H), 7.01–7.90 (4H); δ (N–H), 10.54 (H); δ (NH_2), 8.32 (2H); δ (S–CH_2), 4.04 (4H); 3.60 (8H). δ (S–C–CH_2), 2.24 (12H) $^{13}C\{^1H\}$-NMR: (δ value in ppm) δ (Ar–C), 118.480; δ (S–C), 57.862, 54.682; δ (S–C–C), 25.680, 24.460; δ (C–NH_2), 127.580.

2.1.6. Synthesis of *trans*-dichlorotris(tetramethylenesulphoxide) (2-aminobenzimidazole)ruthenium(II), [*trans*-$RuCl_2(TMSO)_3$(2-ABZ)], (6).

(a) From recrystallized *trans*-$RuCl_2(DMSO)_4$, *trans*-$RuCl_2(TMSO)_4$ was prepared, using the alternative method proposed by Alessio *et al*. [10].

(b) Recrystallized *trans*-$RuCl_2(TMSO)_4$, (0.100 g, 0.00017 mol) was dissolved in 20 mL of ethanol with mild stirring and 2-aminobenizimidazole (0.060 g, 0.00045 mol) dissolved in minimum volume of ethanol was added to the above solution and refluxed for 6 h under inert atmosphere. The solution was concentrated to half by passing a flux of N_2 over hot liquid giving a brown-red complex which was filtered and recrystallized from ethanol/acetone/ether in 5 : 3 : 2, v/v/v and dried in vacuum. Yield 0.068 g (65%). m.p. > 225. Found: C, 36.68; H, 4.98; N, 6.34; S, 15.35; $C_{19}H_{31}N_3S_3O_3Cl_2Ru$ ($M_\tau = 617$) requires C, 36.95; H, 5.05; N, 6.80; S, 15.57; selected infrared absorptions (KBr, cm^{-1}); ν_{SO} 1132(s), 1108(sh); ν_{CN} 1599(s); ν_{Ru-Cl} 329(s); ν_{Ru-S}, 401(m); ν_{Ru-N}, 274(m); $\nu_{(NH)}$, 3443 (m), 3420 (m); electronic spectra (λ_{max}, nm ($\in$ in $M^{-1}\,cm^{-1}$)) in acetone: 445(260); 346(428); 302(625). Δ_M at 25°C($\Omega^{-1}\,cm^2\,mol^{-1}$): 40 in acetone; ^{1}H-NMR spectra: (δ value in ppm) δ (Ar–H), 7.08–8.02 (4H); δ (N–H), 10.52 (H); δ (NH_2), 8.25 (2H); δ (S–CH_2), 3.36 (8H); 3.49 (4H); δ (S–C–CH_2), 3.91(12H). $^{13}C\{^1H\}$-NMR: (δ value in ppm) δ (Ar–C), 116.450; δ (S–C), 54.290, 53.330; δ (S–C–C) 27.662, 25.202; δ (C–NH_2), 126.602.

2.1.7. Synthesis of 2-aminobenzimidazolium *trans*-(2-aminobenzimidazole) (tetramethylenesulphoxide)tetrachloro ruthenate(III), $[2\text{-ABZ}]^+[$*trans*-$Ru(TMSO)(2\text{-ABZ})(Cl_4)]^-$ (7)

(a) Hydrogen *trans-bis*(tetramethylenesulphoxide) tetrachlororuthenate(III) was prepared according to the method of Alessio *et al*. [10].

(b) Recrystallized [(TMSO)H] [*trans*-$Ru(TMSO)_2Cl_4$], (0.100 g, 0.00017 mol) was dissolved in 25 mL of methanol in a two neck flask and 2-aminobenzimidazole (0.055 g, 0.00041 mol) dissolved in 1 N HCl and was added and refluxed for 18 h under inert atmosphere. A purple-black solution was obtained which changes into sticky precipitate on evaporation. This precipitate was recrystallized from methanol/acetone/diethyl ether mixture, and a black precipitate was obtained. Yield 0.080 g (82%). m.p. > 225. Found: C, 39.25; H, 4.80; N, 15.30; S, 5.65; $C_{18}H_{27}N_6SOClRu$ ($M_\tau = 564$) requires C, 39.50; H, 4.90; N, 15.30; S, 5.80; Selected infrared absorption (KBr, cm^{-1}); $\nu_{(CNcyclic)}$, 1596(s); ν_{SO} 1132(s); ν_{Ru-Cl} 330(s); ν_{Ru-S}, 388(m); ν_{Ru-N}, 270(m); $\nu_{(NH)}$, 3445 (m), 3422 (m); Electronic spectra (λ_{max}, nm (ϵ in $M^{-1}cm^{-1}$)) in acetone solution, 330(390); 390(3608); 470(430); $\mu_{eff} = 1.89$; Δ_M at 25°C ($\Omega^{-1}cm^2mol^{-1}$): 102 in acetone and 120 in DMSO.

3. Results and discussion

Stoichiometry of complexes **1–7** are in agreement with elemental analyses. Molecular conductance of **1** and **5** was initially low for a very dilute (10^{-3} M) aqueous solution but increases slowly on keeping the solution for 6–8 h to that for a 1 : 1 electrolyte [1]. Molecular conductance of **2** and **6** was also low initially for a dilute solution, but increases very slowly to that for a 1 : 1 electrolyte on keeping the solution for 5–6 days [1]. Molar conductance of **3**, **4** and **7** was initially that for a 1 : 1 electrolyte, indicating their ionic character [2].

Complex **1**, **2**, **5** and **6** are diamagnetic as expected for low spin ruthenium(II) complexes (low spin, d^6, S = 0). All four complexes exhibit three bands in electronic spectra. The first two bands in **1** and **5** between 361–366 nm and 307–324 nm, may be assigned to d–d transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively, and the band between 250–258 nm can be assigned to the intraligand transition in the coordinated π-acidic imine ligand [11–14]. The bands for **2** and **6** between 445–448 nm and 339.5–346 nm can be assigned to d–d transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively, but the band at lower frequency could be due to a MLCT transition. The band between 299–302 nm is an intraligand transition in the coordinated π-acidic imine ligand [11–14].

Complex **3**, **4** and **7** are paramagnetic with magnetic moments 1.86–1.89 BM, as expected for low spin (d^5) ruthenium(III) complexes. Electronic spectra show three bands in between 470–476 nm, 396–400 nm and 300–330 nm except complex **4**, which has an additional band at 348 nm. The first two bands can be assigned to MLCT transition and the third is assigned to intraligand transitions in the coordinated π-acidic imine ligand [11–14].

FTIR spectra of all the complexes exhibit one or two ν_{SO} between 1090–1132 cm^{-1}. The same band appears at 1055 cm^{-1} in free DMSO and at 1023 cm^{-1} in free TMSO

showing a positive shift in ν_{SO} indicative of the coordination of sulphur to the ruthenium metal center [15, 16]. In all the complexes, a new band appears at 402 cm^{-1} assignable to ν_{M-S}. The heterocyclic ligand contains a sharp band at 1635 cm^{-1}, for cyclic CN vibration, which was shifted to lower wavenumber by ~40 cm^{-1}, clearly indicating coordination of 2-aminobenzimidazole through N^3; appearance of ν_{Ru-N} at ~270 cm^{-1} is in agreement [17, 18]. A very broad band centered at ~728 cm^{-1} observed in **3** and **7** may be attributed to presence of 2-aminobenzimidazolium ion [21, 22]. In almost all the complexes a sharp band at ~330 cm^{-1} with/without a shoulder is assigned to ν_{Ru-Cl} stretching modes. The broad band at ~3440 cm^{-1} has been assigned to ν_{NH}.

All the diamagnetic complexes, **1**, **2**, **5** and **6** were characterized on the basis of ^{1}H-NMR and $^{13}C\{^1H\}$-NMR spectra. The complexes exhibit a signal between δ 7.07–7.82 ppm due to four aromatic protons. A signal appeared at δ ~10.50 ppm for one N–H proton. However, a broad signal centered at ~8.30 ppm for two proton assigned for NH_2 group at almost the same position as in free ligand, proved the non involvement of NH_2 group in coordination. In complex **1** we observed two sets of multiplets centered at δ3.56 and δ3.42. The signal at δ 3.56 ppm for 6 proton was expected for methyl group of the DMSO situated trans to Cl and signal at δ 3.42 ppm was expected for methyl group of DMSO situated trans to each other [9, 23–25]. $^{13}C\{^1H\}$-NMR of this complex shows two signals for methyl carbon of DMSO. The signal at δ 56.28 ppm was expected for the methyl carbon of DMSO trans to Cl, and the signal at δ 54.362 ppm was expected for methyl carbon of the DMSO trans to each other.

In complex **5**, the TMSO analogue, we observed three sets of multiplets centered at δ 2.24, δ 3.60 and δ 4.04 ppm. The signal at δ 4.04 ppm for four protons was expected for S–CH_2 of TMSO ligand situated trans to the Cl atom, while signal at δ 3.6 ppm for 8 protons was expected fot the S–CH_2 proton of the two TMSO ligands trans to each other. The signal at δ 2.24 ppm for 12 protons was expected for the S–C–CH_2 proton of the three TMSO ligands [19, 21, 26].

$^{13}C\{^1H\}$-NMR of **5** shows four signals for methylenic carbons of TMSO. The signal at δ 57.862 ppm was expected for the (S–CH_2) carbon trans to Cl and δ 54.362 ppm was expected for the (S–CH_2) of TMSO trans to each other. The same conclusion can be drawn for signals observed at δ 25.680 ppm and δ 24.680 ppm which were expected for (S–C–CH_2) methylenic carbon of the TMSO.

The signals for aromatic carbon were centered between δ 116.484–119.491 ppm; resonance for the amino carbon (C–NH_2) remained unshifted in the complex, indicating non-involvement of NH_2 group in coordination.

Thus, on the basis of FTIR, UV-VIS, ^{1}H-NMR and $^{13}C\{^1H\}$-NMR the most plausible structures for **1** and **5** are shown in figure 1.

In **2**, the DMSO analogue, we observed two sets of multiplets centered at δ 3.46 and δ 3.58 ppm, which corresponds to S-bonded DMSO. The relative intensity of the two is 2 : 1 suggesting that two DMSO's are trans to each other and another is trans to the 2-aminobenzimidazole ligand [9, 23–25]. $^{13}C\{^1H\}$-NMR of this complex shows two signals for methyl carbon of DMSO, at δ 54.268 ppm for the methyl carbon trans to Cl and at δ 52.697 ppm for methyl carbon of the DMSO trans to benzimidazole.

In **6**, the TMSO analogue, we observed three sets of multiplets centered at δ 3.36, δ 3.49 and δ 3.94 ppm. The signal at δ 3.36 ppm for eight protons was expected for S–CH_2

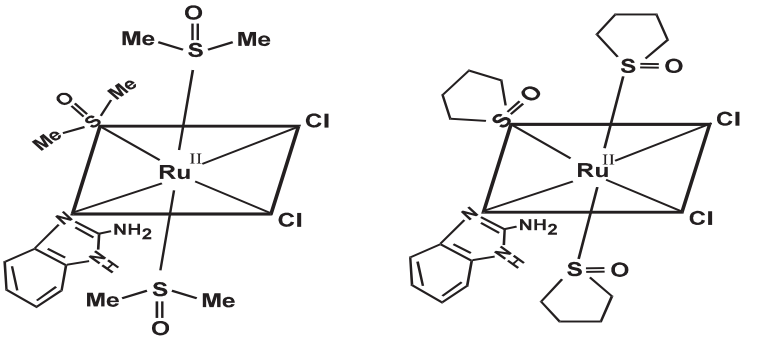

Figure 1. Structures of **1** and **5**.

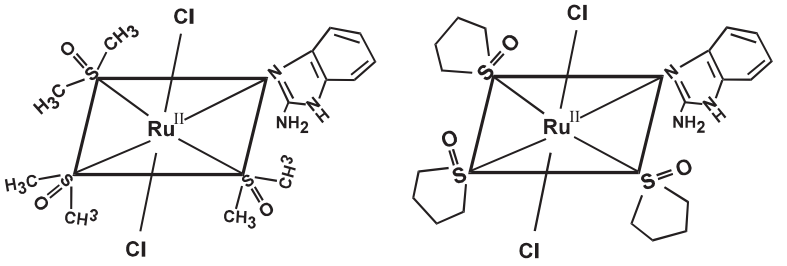

Figure 2. Structures of **2** and **6**.

proton of TMSO ligand situated trans to each other, δ 3.49 ppm for four protons was expected for S-CH_2 proton of TMSO situated trans to 2-aminobenzimidazole ligand, however a signal centered at 3.49 ppm for 12 protons was expected [19–21, 26].

$^{13}C\{^1H\}$-NMR of **6** shows four signals for methylenic carbons of TMSO; δ 54.290 ppm for the (S–CH_2) of TMSO's trans to each other, δ 53.330 ppm for TMSO trans to benzimidazole unit. Same conclusion can be inferred for δ 27.660 and δ 25.202 ppm which were expected for (S–C–CH_2) methylenic carbons of TMSO.

In both complexes resonances the aromatic carbons were centered between δ 116.450–118.480 ppm; similar signals for amino carbon (C–NH_2) at the same position as for free ligand, indicate non-involvement of NH_2 group in coordination. Thus, on the basis of FTIR, UV-VIS, ^{1}H-NMR and $^{13}C\{^1H\}$-NMR we suggest structures for **2** and **6** as shown in figure 2.

On the basis of FTIR, UV-VIS and elemental analyses we suggest structures for **3**, **4** and **7** as shown in figure 3.

4. Conclusion

We have prepared seven complexes of ruthenium(II) and ruthenium(III) containing dimethylsulphoxide/tetramethylenesulphoxide with 2-aminobenzimidazole which may

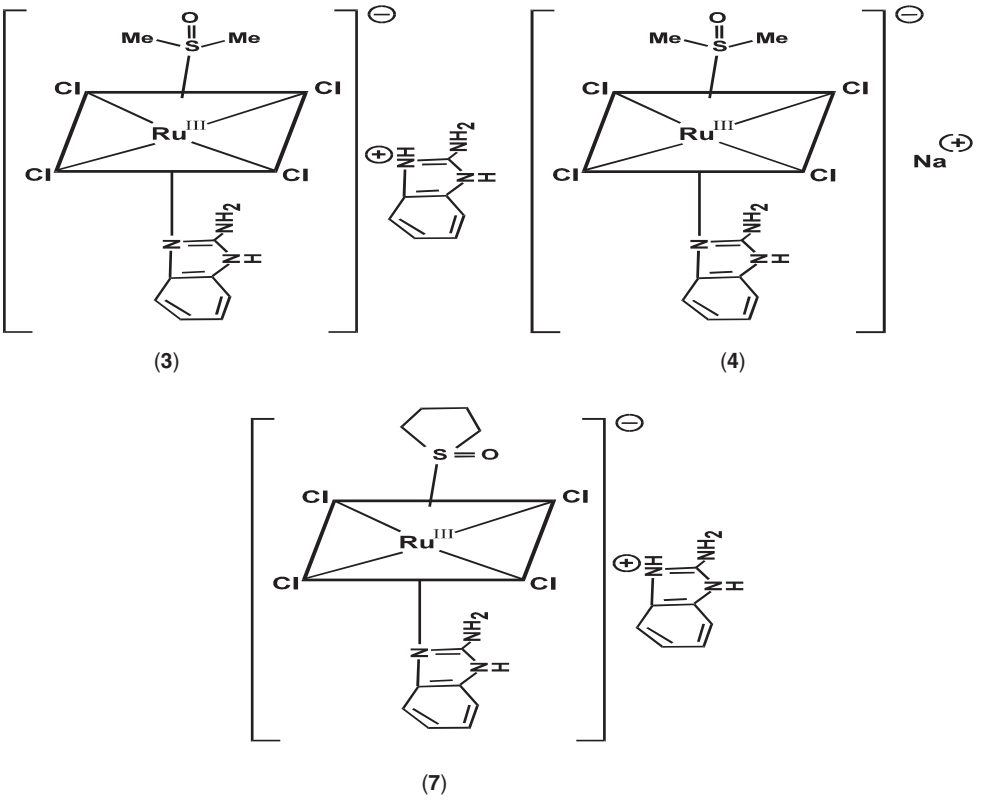

Figure 3. Suggested structures of **3**, **4**, and 7.

find importance due to their biological activity. Their characterization and chemical reactivity give a new look to Ru(II) and Ru(III)-DMSO/TMSO derivatives.

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