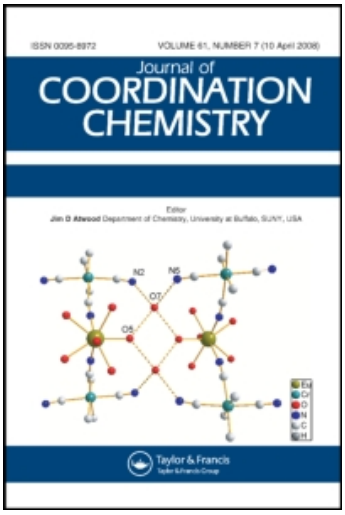

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Synthesis, spectroscopic characterization and antibacterial sensitivity of some chloro dimethylsulfoxide/tetramethylenesulfoxide ruthenium(II) and ruthenium(III) complexes with 2-aminobenzothiazole

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Synthesis, spectroscopic characterization and antibacterial sensitivity of some chloro dimethylsulfoxide/ tetramethylenesulfoxide ruthenium(II) and ruthenium(III) complexes with 2-aminobenzothiazole

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Synthesis and characterization of seven ruthenium(II) and ruthenium(III) complexes of sulfoxide with 2-aminobenzothiazole are reported. Three different formulations exist: [*cis*,*cis*,*cis*-$RuCl_2(SO)_2$(2-abtz)$_2$] and [*trans*,*trans*,*trans*-$RuCl_2(SO)_2$(2-abtz)$_2$] and [*trans*-$RuCl_4$(SO)(2-abtz)]$^-$ $[X]^+$ (where SO = dimethyl sulfoxide (dmso) or tetramethylenesulfoxide (tmso); 2-abtz = 2-aminobenzothiazole and $[X]^+ = [H(abtz)]^+$, $[Na^+]$. These complexes were characterized by elemental analyses, conductivity measurements, magnetic susceptibility, FTIR, ^{1}H NMR, $^{13}C\{^1H\}$ NMR and electronic spectroscopy. Some of the complexes were screened for their antibacterial activity and are found to be potent against the gram negative bacteria *Escherichia coli*.

Keywords: Ruthenium; Dimethylsulfoxide; Tetramethylenesulfoxide; Aminobenzothiazole

1. Introduction

Some ruthenium compounds have proved to have noteworthy pharmacological profiles [1]. The good antitumor property and remarkably low cytotoxicity make them effective against tumors that are resistant to cisplatin and carboplatin [2]. Two ruthenium(III) compounds, K1019, {[InH][*trans*-$RuCl_4(Ind)_2$]}, Ind = Indazole, developed by Keppler *et al.* [3, 4], is active against colorectal tumors [5] and NAMI-A, {[ImH][*trans*-$RuCl_4$(dmso-S)(Im)]}, Im = imidazole, developed by Alessio, Sava *et al.* is active against metastasis of solid tumor [6–8]. NAMI-A has completed a Phase-I trial and is scheduled to begin phase-II trials soon [9], while K1019 is currently in phase-I trials [10].

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Interest has been centered around the catalytic property on high and low valent ruthenium complexes [11]. Various useful catalytic reactions have also been explored [12]. Ruthenium complexes are highly useful redox Lewis acid and base catalysts [16]. The versatility of ruthenium sulfoxide complexes has prompted us to explore the synthesis of some new complexes with biologically active heterocyclic ligands. Inspired by our previous study on 2-aminobenzimidazole derivatives of halo ruthenium sulfoxides [14], and since substituted benzothiazole are very effective to inhibit the growth of different bacteria at minimum inhibitory concentrations [15], here we have studied reaction of 2-aminobenzothiazole with ruthenium sulfoxides.

2. Experimental

$RuCl_3 \cdot 3H_2O$ (E. Merck), 2-aminobenzothiazole and tetramethylene sulfoxide (Lancaster, UK) were used as received and analytical grade dimethylsulfoxide (BDH) and solvents were used without further purification for syntheses. Electronic absorption spectra were recorded with a Systronics-2201, double beam spectrophotometer equipped with a PC. Conductivity measurements were carried out at 25°C on an Elico CM-180 conductivity bridge with dipping type cell. FTIR spectra were recorded in KBr pellets on a Nicolate magna-750 FTIR spectrophotometer. ^1H NMR and $^{13}C\{^1H\}$ NMR spectra were recorded in dmso-d_6 on a Bruker DRX-400 MHz 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. Yields were calculated on the basis of empirical formula.

2.1. *Synthesis of complexes*

2.1.1. Synthesis of [*cis*,*cis*,*cis*-$RuCl_2(dmso)_2(2\text{-abtz})_2$], (1). Recrystallized *cis*-$RuCl_2(dmso)_4$ (0.100 g, 0.20 mmol) is dissolved in acetone. To this solution 2-aminobenzothiazole (0.080 g, 0.52 mmol) was added and the reaction mixture was stirred for 7 h. The transparent solution was reduced to half of its volume under reduced pressure and kept overnight. A dark red precipitate was obtained, which was washed several times with acetone/diethyl ether (1 : 1) and further purified by column chromatography using silica gel (60–120 mesh). Eluting the column isolated the red product by a 1 : 1 v/v acetone–methanol mixture. Evaporation of solvent from the eluate yielded a red solid. Yield: 0.050 g (62%). M.p. >225°C. Found: C, 34.29; H, 3.80; N, 8.90; S, 20.32; $C_{18}H_{24}N_4O_2S_4Cl_2Ru$ ($M_\tau = 628$). Requires C, 34.31; H, 3.82; N, 8.91; S, 20.38. Selected infrared absorption (KBr, cm^{-1}); ν_{SO} 1115(s); ν_{Ru-Cl} 340(s), 320(sh); $\nu_{(CNcyclic)}$ 1612(s); $\nu_{(N-H)}$ 3451(m); ν_{Ru-S} 402(m); ν_{Ru-N} 282(s); Electronic spectra (λ_{max}, nm ($\in$ in $M^{-1}\,cm^{-1}$)) in acetone solution: 667(18), 553(26), 376(806), 336(906), 254(1010), 212(960); in methanol solution: 638(42), 540(65), 390(2664), 340(2777), 260(2900). Δ_M at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$); 55 in dmso. ^1H NMR spectra (δ value in ppm): δ(Ar–H), 7.02–7.82 (8H, m); $\delta(NH_2)$, 6.05–6.87 (4H, brs); $\delta(CH_3)$, 3.25 (6H, s), 2.63(6H, s); $^{13}C\{^1H\}$ NMR (δ value in ppm): δ(Ar–C), 119.39(m) 131.73(m); δ(S–CH_3), 56.52(s), 53.96(s); δ(C–NH_2), 165.61(s), 165.86(s).

2.1.2. Synthesis of [*trans*,*trans*,*trans*-$RuCl_2(dmso)_2(abtz)_2$], (2). Recrystallized *trans*-$RuCl_2(dmso)_4$ [13] (0.060 g, 0.12 mmol) was dissolved in acetone. To this solution 2-aminobenzothiazole (0.050 g, 0.33 mmol) was added and the reaction mixture was kept under constant stirring and reflux for 6 h. A dark yellow–brown sticky precipitate was obtained, which was washed several times with acetone and diethyl ether and then dissolved in minimum quantity of ethanol. A yellow brown solid was obtained by passing this into a very dilute solution of NaCl in water with continuous stirring, filtered and washed several times with water and recrystallized from acetone–methanol–water 3 : 2 : 1, (v/v) mixture. Yield: 0.060 g (77%). M.p. >225°C. Found: C, 34.38; H, 3.82; N, 8.93; S, 20.39. $C_{18}H_{24}N_4O_2S_4Cl_2Ru$ ($M_\tau = 628$). Requires C, 34.31; H, 3.82; N, 8.91; S, 20.38. Selected infrared absorption (KBr, cm^{-1}); ν_{SO} 1115(s); $\nu_{Ru–Cl}$ 345(s), 326; $\nu_{(CNcyclic)}$ 1620; $\nu_{(N–H)}$ 3455(m); $\nu_{Ru–S}$ 398(m); $\nu_{Ru–N}$ 276(m). Electronic spectra (λ_{max}, nm (ϵ in $M^{-1}\,cm^{-1}$)) in acetone solution: 667(15), 450(860), 345(920), 300(750), 212(908); in methanol solution: 656(52), 667(15), 460(54), 360(1219), 322(1326), 226(1805). Δ_M at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$); 49 in acetone. ^1H NMR spectra (δ value in ppm): δ(Ar–H), 7.02–7.82 (8H, m); $\delta(NH_2)$, 6.05–6.87 (4H, brs); $\delta(CH_3)$, 3.46 (12H, s); $^{13}C\{^1H\}$ NMR (δ value in ppm): δ(Ar–C), 120.39–135.68(m); δ(C–NH_2), 168.69(s); δ(S–CH_3), 56.268(s).

2.1.3. Synthesis of $[H(abtz)]^+[$*trans*-$RuCl_4(abtz)(dmso)]^-$, (3). Recrystallized $[H(dmso)_2][$*trans*-$RuCl_4(dmso)_2]$ [17] (0.080 g, 0.14 mmol) was dissolved in 20 mL acetone. To this solution 2-aminobenzothiazole (0.054 g, 0.35 mmol) in acetone was added and the reaction mixture was kept under stirring for 8 h in an inert atmosphere. The brown solution obtained was concentrated under reduced pressure to half of its volume and kept overnight under inert atmosphere. A dark brown precipitate was obtained, filtered and recrystallized from 1 : 2 ethanol–acetone (v/v). Yield: 0.060 g (67%), M.p. >225°C. Found: C, 30.82; H, 3.07; N, 9.05; S, 15.49. $C_{16}H_{19}N_4OS_3Cl_4Ru$ ($M_\tau = 622$). Requires C, 30.86; H, 3.05; N, 9.00; S, 15.43. Selected infrared absorptions (KBr, cm^{-1}); ν_{SO} 1110(s); $\nu_{Ru–Cl}$ 339(s); $\nu_{(CNcyclic)}$ 1602(s); $\nu_{(Ru–Cl)}$ 339(s); $\nu_{Ru–N}$ 285(m); $\nu_{Ru–S}$ 409(m); $\nu_{(N–H)}$ 3450(m), 750(br). Electronic spectra (λ_{max}, nm (ϵ in $M^{-1}\,cm^{-1}$)) in dmso: 624(36), 478(702), 430(980), 300(603), 210(506); in methanol: 646(26), 490(683), 450(886), 296(704); $\mu_{eff} = 1.92\,\mu B$. Δ_M at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 108 in dmso.

2.1.4. Synthesis of Na[*trans*-$RuCl_4$(2-abtz)(dmso-S)], (4). To recrystallized Na[*trans*-$RuCl_4(dmso)_2$] [18] (0.030 g, 0.07 mmol) dissolved in 4 mL dimethylsulfoxide was added 2-aminobenzothiazole (0.024 g, 0.15 mmol) dissolved in acetone and the reaction mixture was kept under stirring for 7 h, followed by reflux for 2 h. A greenish precipitate was obtained after concentrating the reaction mixture under reduced pressure. The solid was recrystallized from acetone–methanol 3 : 2 v/v. Yield: 0.030 g (85%), M.p. >225°C. Found: C, 21.75; H, 2.41; N, 5.62; S, 12.95. $C_9H_{12}N_2S_2OCl_4NaRu$ ($M_\tau = 493$). Requires C, 21.90; H, 2.43; N, 5.67; S, 12.98. Selected infrared absorptions (KBr, cm^{-1}); ν_{SO} 1102(s); $\nu_{Ru–Cl}$ 334(s); $\nu_{Ru–S}$ 400(m); $\nu_{Ru–N}$ 280(s); $\nu_{(N–H)}$ 3450(m), 3435 (m); ν_{CN} 1606(s); Electronic spectra (λ_{max}, nm (ϵ in $M^{-1}\,cm^{-1}$)) in dmso: 624(37), 482(506), 426(926), 212(606); in methanol: 496(308), 640(24), 440(876), 220(960); $\mu_{eff} = 1.89\,\mu B$, Δ_M at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 110 in dmso.

2.1.5. Synthesis of [*cis*,*cis*-$RuCl_2(tmso)_2(2\text{-abtz})_2$], (5). Recrystallized [*cis*-$RuCl_2(tmso)_4$] [13] (0.050 g, 0.08 mmol) was dissolved in acetone and to this solution 2-aminobenzothiazole (0.030 g, 0.19 mmol) was added. The reaction mixture was kept under constant stirring for 7–8 h in an inert atmosphere. The solution was concentrated under reduced pressure until a violet precipitate appears, which was filtered and recrystallized from acetone–chloroform–ethanol 1 : 2 : 3 (v/v). Yield: 0.050 g (87%), M.p. >225°C. Found: C, 38.80; H, 4.09; N, 8.20; S, 18.81. $C_{12}H_{28}N_4O_2S_4Cl_2Ru$ ($M_\tau = 680$). Requires C, 38.82; H, 4.11; N, 8.23; S, 18.82. Selected infrared absorptions (KBr, cm^{-1}); ν_{SO} 1122(s); ν_{Ru-Cl} 326(s), 330(m); ν_{Ru-N} 276(s); ν_{Ru-S} 402(s); $\nu_{(CNcyclic)}$ 1604; $\nu_{(N-H)}$ 3451(m). Electronic spectra (λ_{max}, nm ($\in$ in $M^{-1}\,cm^{-1}$)) in acetone solution: 642(32), 538(56), 370(560), 302(400), 252(806), 210(900); in methanol: 622(40), 556(60), 390(465), 315(425), 270(908). ^1H NMR spectra (δ value in ppm); δ(Ar–H), 7.07–7.82 (8H, m); $\delta(NH_2)$, 6.00–6.89 (4H, brs); $\delta(S\text{–}CH_2)$, 3.25 (4H, s), 3.03 (4H, s); $\delta(S\text{–}C\text{–}CH_2)$, 2.52 (8H, s). $^{13}C\{^1H\}$ NMR spectra (δ value in ppm): δ(Ar–C), 110.68–132.63(m); $\delta(S\text{–}CH_2)$, 57.862(s), 54.362(s); $\delta(C\text{–}NH_2)$, 165.61(s), 165.92(s); $\delta(S\text{–}C\text{–}CH_2)$, 26.628(s), 25.320(s).

2.1.6. Synthesis of [*trans*,*trans*,*trans*-$RuCl_2(tmso)_2(2\text{-abtz})_2$], (6). Recrystallized [*trans*-$RuCl_2(tmso)_4$] [17] (0.100 g, 0.16 mmol) was dissolved in acetone. To this solution 2-aminobenzothiazole (0.070 g, 0.4 mmol) was added and the reaction mixture was kept under stirring for 7 h in an inert atmosphere. A black brown precipitate was obtained after concentrating the reaction mixture under reduced pressure. The solid was recrystallized from acetone–choloroform–methanol 1 : 2 : 3 v/v. Yield: 0.060 g (54%), M.p. >225°C. Found: C, 38.80; H, 4.10; N, 8.20; S, 18.79. $C_{22}H_{28}N_4O_2S_4Cl_2Ru$ ($M_\tau = 680$). Requires C, 38.82; H, 4.11; N, 8.23; S, 18.82. Selected infrared absorptions (KBr, cm^{-1}); ν_{SO} 1115; ν_{Ru-Cl} 330(s), 334(m); $\nu_{(CNcyclic)}$ 1604; $\nu_{(N-H)}$ 3452(m); ν_{Ru-S} 402(m); ν_{Ru-N} 286(s). Electronic spectra (λ_{max}, nm ($\in$ in $M^{-1}\,cm^{-1}$)) in acetone solution: 662(22), 452(302), 356(486), 296(636); in methanol: 646(36), 450(553), 365(1126), 306(1384). Δ_M at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 48 in acetone. ^1H NMR spectra (δ value in ppm: δ(Ar–H), 7.12–7.84 (8H, m); $\delta(NH_2)$, 6.082–6.68 (4H, brs); $\delta(S\text{–}CH_2)$, 3.06 (8H, s); $\delta(S\text{–}C\text{–}CH_2)$, 2.63 (8H, s). $^{13}C\{^1H\}$ NMR spectra (δ value in ppm): δ(Ar–C), 122.69–135.73(m); $\delta(S\text{–}CH_2)$, 54.290(s); $\delta(S\text{–}C\text{–}CH_2)$, 25.260(s).

2.1.7. Synthesis of $[H(abtz)]^+$[*trans*-$RuCl_4(abtz)(tmso)]^-$, (7). To the recrystallized [H(tmso)][*trans*-$RuCl_4(tmso)_2$] [19] (0.050 g, 0.89 mmol) dissolved in acetone was added 2-aminobenzothiazole (0.033 g, 0.22 mmol) and the reaction mixture was stirred for 9 h under an inert atmosphere and then refluxed for 1 h. A dark brown precipitate was obtained and recrystallized from acetone–ethanol 1 : 3 (v/v). Yield: 0.050 g (86%), M.p. >225°C. Found: C, 33.30; H, 3.29; N, 8.62; S, 14.80. $C_{18}H_{21}N_4OS_3Cl_4Ru$ ($M_\tau = 648$). Requires C, 33.33; H, 3.24; N, 8.64; S, 14.81. Selected infrared absorptions (KBr, cm^{-1}); ν_{SO} 1120; ν_{CN} 1599(s); ν_{Ru-Cl} 321(s); ν_{Ru-S} 340(m); ν_{Ru-N} 273; $\nu_{(N-H)}$ 3450(m), 3430(m). Electronic spectra (λ_{max}, nm ($\in$ in $M^{-1}\,cm^{-1}$)) in acetone solution: 620(20), 460(500), 418(630), 308(810), 216(589); in methanol: 648(16), 472(624), 436(703), 318(860); $\mu_{eff} = 1.94\,\mu B$. Δ_M at 25°C ($\Omega^{-1}\,cm^2\,mol^{-1}$): 110 in acetone and 140 in dmso.

3. Results and discussion

Empirical formula of **1**–**7** are in conformity of the elemental analyses. Molar conductance of **1**, **2**, **5** and **6** was low for a very dilute solution (10^{-3} M) probably due to their non-electrolytic nature. However, molar conductance of **3**, **4** and **7** was higher indicating their ionic nature [18].

Complexes **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 five bands in the electronic spectra. In **1** and **5** the first two bands between 622–667 nm and 538–556 nm with a very low extinction coefficient, may be assigned to d–d transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively. The bands between 370–390 nm and 302–340 nm may be attributed to the MLCT transitions. The band at 250 nm can be assigned to intraligand transitions in the coordinated π-acidic imine ligand [20–23]. The band at 210 nm was probably due to the presence of sulfoxide [32].

In **2** and **6**, the bands at 650 nm and 450 nm can be assigned to d–d transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively, but the second band may have contribution from MLCT transitions. The band at about 300 nm is assigned to intraligand transitions in the coordinated π-acidic imine ligand [20–23]. Here, also a band at 220 nm was observed and assigned to the presence of sulfoxide [32].

Complexes **3**, **4** and **7** are paramagnetic with magnetic moments between 1.89–1.94 BM as expected for low spin (d^5) ruthenium(III) complexes. Electronic spectra of these complexes show four/five bands a fifth band appeared at about 640 nm with a very low extinction coefficient. The band with high optical density, at about 426 nm coupled with less intense band at λ_{max} 476 nm, is ascribed to a charge transfer transition from chlorides to Ru(III), a typical identification for $RuCl_4^-$ [33]. In addition a weak absorption band at about 300 nm in **3** and **7** is probably due to the presence of protonated cation. However, a band at about 210 nm for sulfoxide is also present [32].

FTIR spectra of **1**–**7** exhibit one or two sharp bands for ν_{SO} in between 1102–1120 cm^{-1}. This band, which appears at 1055 cm^{-1} in free dmso and at 1023 cm^{-1} in free tmso, shows a positive shift in ν_{SO}, an indication of coordination of sulfur to the ruthenium [24, 25]. In all the complexes a new band at about 400 cm^{-1} assigned for ν_{Ru-S} confirms this interpretation. The heterocyclic ligand contains a sharp band at 1644 cm^{-1}, for cyclic CN_{str}, which shifted to lower wavenumber by ~20–40 cm^{-1}, clearly indicating coordination of 2-aminobenzothiazole through N^3 of cyclic (C=N) [30, 31]. Appearance of ν_{Ru-N} at ~275 cm^{-1} supports this. A very broad band at ~755 cm^{-1} observed only in **3** and **7**, may be attributed to the presence of 2-aminobenzothiazolium ion [27, 28]. In all the complexes, a sharp band at ~330 cm^{-1} is assigned to ν_{Ru-Cl} stretch. The broad band at ~3450 cm^{-1} is assigned for ν_{NH}.

All the diamagnetic complexes, **1**, **2**, **5** and **6**, were characterized on the basis of ^1H NMR and $^{13}C\{^1H\}$ NMR spectra. These complexes exhibit a multiplet between δ 7.02–7.88 ppm due to eight aromatic protons. A signal between δ 6.00–6.89 ppm for four protons attributed to NH_2, which was observed almost at the same position as in the ligand, suggested the non-involvement of NH_2 in coordination to metal.

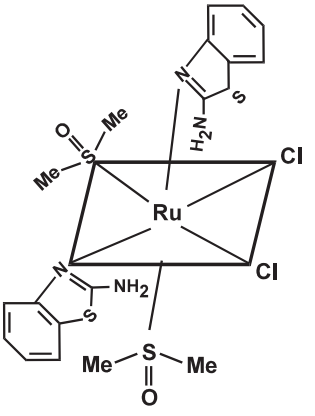
In **1**, we observed two sets of multiplets centered at δ 3.25 and δ 3.02 ppm. The signal at δ 3.25 ppm for six protons was assigned to methyl of dmso *trans* to Cl and the signal at δ 3.02 ppm was assigned to methyl of dmso *trans* to aminobenzothiazole.

The relative intensity of resonance is 4 : 1 : 6, suggesting that two molecules of dmso are replaced by 2-aminobenzothiazole.

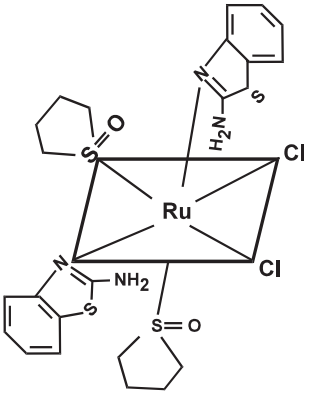
However, in **5**, the tmso analogue, we observed three multiplets centered at δ 3.25, δ 3.03 and δ 2.52 ppm. The signal at δ 3.25 ppm for four protons was assigned to S–CH_2 of tmso *trans* to Cl, while signal at δ 3.03 ppm (4H) was assigned to S–CH_2 of tmso *trans* to 2-aminobenzothiazole. Resonance at δ 2.52 ppm (8H) was assigned to S–C–CH_2 of both tmso's [26, 27, 29].

$^{13}C\{^1H\}$ NMR of **1** shows two signals for methyl of dmso. The signal at δ 56.28 ppm was assigned for the methyl carbon *trans* to Cl, and the singlet at δ 54.36 ppm was assigned for methyl of dmso *trans* to 2-aminobenzothiazole. However, $^{13}C\{^1H\}$ NMR of **5** shows four signals for methylene carbons of tmso. The signal at δ 57.86 ppm was assigned to (S–CH_2) of tmso *trans* to Cl; the signal at δ 54.36 ppm was assigned (S–CH_2) of tmso *trans* to 2-aminobenzothiazole; signal at δ 26.62 ppm was assigned for S–C–CH_2 of tmso *trans* to Cl; the other signal observed at δ 25.32 ppm was assigned to (S–C–CH_2) carbon *trans* to 2-aminobenzothiazole. In the $^{13}C\{^1H\}$ NMR a multiplet was observed between δ 118.68–135.73 ppm in all the complexes and assigned for aromatic carbons. Similarly, a signal observed about δ 165 ppm, almost the same as in the ligand, indicated non-involvement of NH_2 in coordination. However, in **1** and **5**, this signal surprisingly splits in to two at δ 165.86 and δ 165.61 ppm for dmso and δ 165.92 and δ 165.61 ppm in the tmso analogue. This splitting was probably due to the presence of Cl *trans* to one 2-aminobenzothiazole and tmso/dmso to another 2-aminobenzothiazole unit.

Thus, on the basis of FTIR, UV-vis, ^1H NMR and $^{13}C\{^1H\}$ NMR, the most plausible structures for **1** and **5** are:



(1)



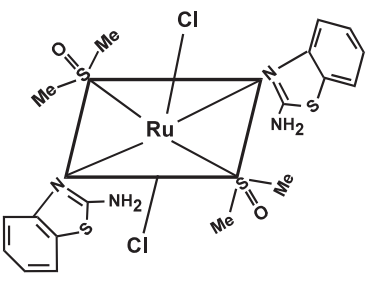
(5)

In **2**, we observed only one signal in this ^1H NMR centered at δ 3.46 for 12 protons, assigned to methyls of dmso, indicating that the two dmso's are in same environment. This was further confirmed by $^{13}C\{^1H\}$ NMR with one resonance at δ 56.26 ppm assigned to all four methyl's of dmso's.

In **6**, in the tmso analogue, we observed two sets of signals centered at δ 3.06 ppm and δ 2.63 ppm in the ^1H NMR. The signal at δ 3.06 ppm (8H) was assigned to S–CH_2 proton of the two tmso's *trans* to each other and the signal at δ 2.63 ppm (8H) was assigned to S–C–CH_2 of the tmso's. $^{13}C\{^1H\}$ NMR of this complex shows two signals

at δ 54.29 ppm, assigned for (S–CH_2) carbon of tmso, and at δ 25.26 ppm, assigned to (S–C–CH_2) carbon of tmso.

Thus, on the basis of FTIR, UV-VIS, ^{1}H NMR and $^{13}C\{^1H\}$ NMR, we suggest the most plausible structures for **2** and **6**.



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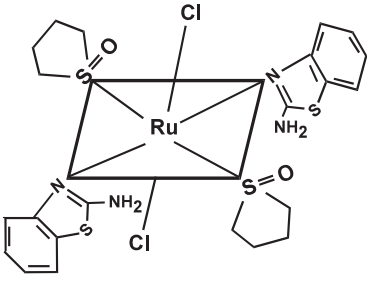
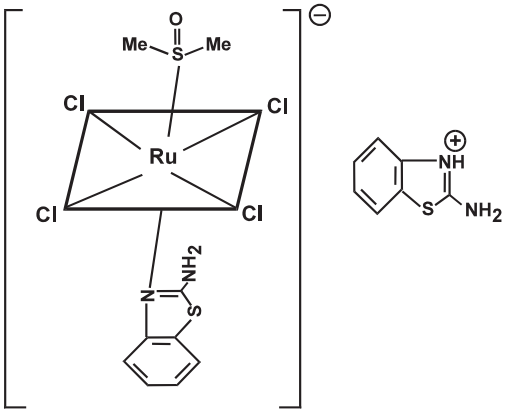
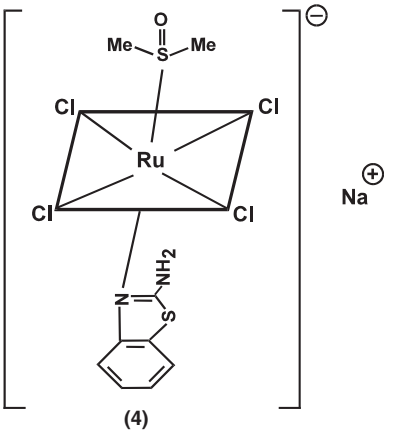


(6)

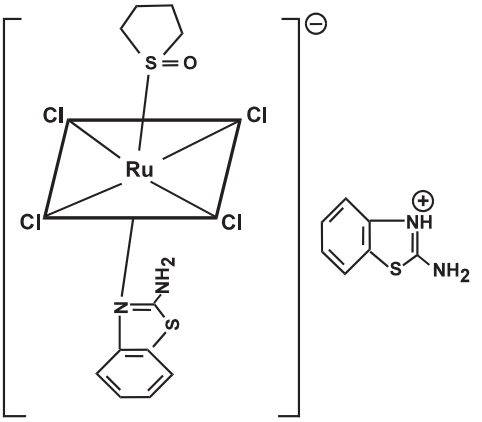
The signals in NMR spectra of **3**, **4** and **7** were broad and severely shifted due to the paramagnetic ion and we are not able to use NMR as a diagnostic tool in these complexes.



(3)



(4)



(7)

Table 1. Antibacterial sensitivity test against *Escherichia coli*.

Compound/Sample	Sensitivity against *E. coli*
Sample A (2-abtz)	−
Compound **1**	+
Compound **3**	+
Compound **5**	+
Compound **7**	+
Solvent (dmso)	−

*Zone diameter of inhibition >8 mm is taken as sensitive and shown as + in the table; − denotes insensitive.

Thus, on the basis of FTIR, UV-vis and elemental analyses we suggest probable structures for **3**, **4** and **7**.

3.1. *Antibacterial activity*

Antibacterial activity of **A** (where **A** = 2-aminobenzothiazole), **1**, **3**, **5**, and **7** have been tested on *E. coli* MTCC 1304, a gram-negative bacteria (table 1). Muller Hinton Agar (MHA) plates were prepared and 50 µL suspension of *E. coli* MTCC 1304 was spread over it by spread plate technique [37], and then wells were made for 50 µL solution of 0.2% of above samples along with 2-aminobenzothiazole (dissolved in dmso). One plate is used as control, in which only 50 µl dmso is taken into the well. These plates were incubated at 37 ± 1°C for 24–48 h in a refrigerated incubator shaker. The result shows no inhibition zone observed around the control and **A**, but **1**, **3**, **5** and **7** showed inhibition zone formation around the well. *Escherichia coli* MTCC 1304 grew over the well of the control and **A**, but no growth was seen in the well of samples for **1**, **3**, **5** and **7**. Thus, all complexes show enhanced antibacterial activity over the ligand, probably due to enhanced lipophilicity of the complexes [35, 36, 32]. This increased lipophilicity leads to breakdown of the permeability barrier of the cell and thus retards the normal cell process.

4. Conclusion

We have prepared seven complexes of ruthenium(II)/ruthenium(III) dimethyl/tetramethylenesulfoxide with 2-aminobenzothiazole. These complexes require further biological screening at lower dilution and may find more importance in the future due to other aspects of biological activity. Their characterization, reactivity and inherent biological activity throws new light on ruthenium(II) and ruthenium(III) based pharmaceuticals.

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