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Synthesis, Spectroscopic Characterization and Antibacterial Activity of some Chloro Dimethylsulphoxide/ Tetramethylenesulphoxide Ruthenium (II)/(III) Complexes with 1, 2, 3-Benzotriazole

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Abstract

Synthesis and characterization of seven ruthenium (II) and ruthenium (III) chloro sulphoxide complexes with 1, 2, 3-benzotriazole are reported. Three different formulations exist: [cis,fac–$RuCl_2(so)_3(btz)$]; [trans–$RuCl_2(so)_3(btz)$] and [trans–$RuCl_4(so)(btz)]^-[X]^+$; where so=dimethylsulphoxide/ tetramethylenesulphoxide; btz = 1, 2, 3-benzotriazole and $[X]^+ = [(btz)H]^+$ or Na^+. These complexes were characterized by elemental analysis, conductivity measurements, magnetic susceptibility, FT-IR, ^{1}H-NMR, $^{13}C\{^1H\}$-NMR and electronic spectroscopy. Complexes were screened for their antibacterial activity and found more potent than 1, 2, 3-benzotriazole ligand and precursor ruthenium compounds against gram-negative bacteria *Escherichia coli.* All the samples were compared with antibiotic Chloramphenicol for reference.

Keywords: Benzotriazole, dimethylsulphoxide, ruthenium, tetramethylenesulphoxide.

1. Introduction

Ruthenium compounds represent a new class of compounds endowed with antitumour activity. The NAMI–A; $\{[ImH]^+$ $[trans\text{-}RuCl_4(Im)(DMSO\text{-}S)]^-$, Imidazoliumtrans-imidazoledimethylsulphoxidetetrachlororuthenate(III) is one of them and characterized against lung metastasis of solid mouse tumours and human xenograft.[1–3] The KP1019, $\{[InH]^+$ $[trans–RuCl_4(Ind)_2]^-\}$ developed by Keppler *et al.* is active against colorectal tumours.[4–6] NAMI-A has completed a phase–I and phase–II trials soon,[7] while KP1019 is currently in phase–I trials.[8]

Despite these noteworthy contribution as anticancer pharmacological profiles, ruthenium compounds are recently screened for their antibacterial and antifungal activity against a range of plant and human pathogen.[9] Ruthenium complexes are well suited to medicinal use because of their rate of ligand exchange, range of accessible oxidation state and ability of ruthenium to mimic iron in binding to certain biological molecule such as transferrin.[10, 11]

In view of our previous study[12–14] we sought to characterize here some more ruthenium sulphoxide complexes coupled with N-donor heterocyclic ligand 1,2,3-benzotriazole. The benzotriazole derivatives have been implicated as possible carcinogens, endocrine disempters, and plant hormone regulators.[15]

2. Experimental

$RuCl_3.3H_2O$ (E. Merck), 1, 2, 3-benzotriazole (spectrochem) and tetramethylenesulphoxide (Lancaster, U.K.)

were used as received and analytical grade dimethylsulphoxide (E. Merck) and solvents were used without further purification for synthetic purpose. Electronic absorption spectra were recorded with systronics–2201, double beam spectrophotometer equipped with a PC. Conductivity measurements were carried out at 25 °C on an EI conductivity bridge with a dipping type cell. FT-IR spectra were recorded in KBr on Nicolet Magna-750 FT-IR spectrophotometer. Far IR spectra were measured in CsI Perkin Elmer RX1 spectrophotometer. ^{1}H-NMR spectra and ^{13}C{^{1}H}-NMR spectra were recorded in dmso-d_6 on Bruker 400 MHz spectrometer. Chem Draw Ultra 8.0 software has been used in preparation of molecular structure. Gouy's method was employed for measurement of magnetic susceptibility. Cobalt mercurytetrathiocyanate was used as standard. Diamagnetic correction was made using Pascal's constant.

2. 1. Synthesis of Complexes

2. 1. 1. Synthesis of [*cis*,*fac*-$RuCl_2$ $(S\text{-}DMSO)_3(btz)$], Complex (1)

(a) [*Cis*,*fac*-$RuCl_2(S\text{-}DMSO)_3(O\text{-}DMSO)$] was prepared according to literature cited.[16]

(b) Recrystallized [*cis*,*fac*-$RuCl_2(S\text{-}DMSO)_3(O\text{-}DMSO)$], (0.050 g, 0.1 mmol) was dissolved in 20 mL of acetone. Benzotriazole (0.024 g, 0.2 mmol) dissolved in minimum volume (5 mL) of acetone was added and the reaction mixture was stirred for 7 h. The yellow precipitate was obtained which was washed several times with acetone/diethyl ether, (1:1), (v/v) solvent mixture and dried in vacuum. Yield: 0.047 g (87%). M.p. > 225 °C. Found: C, 27.40; H, 4.35; N, 8.02; S, 18.25; $C_{12}H_{23}N_3O_3S_3Cl_2Ru$ (Mτ = 525). Require(s): C, 27.42; H, 4.38; N, 8.00; S, 18.28. Selected infrared absorptions (KBr, cm^{-1}): ν(N-H), 3447.6(m); ν(N=N), 1410(s); ν(SO), 1097(s), 1091(m); ν(Ru-S), 402(m); ν(Ru-Cl), 335(s), 330(sh); ν(Ru-N), 282(s). Electronic spectra (λ max, nm (ε in M^{-1} cm^{-1})): in acetonitrile solution, 650(30), 540(38), 380(1886), 345(1508), 280(2006). Δm at 25 °C (Ω^{-1} cm^2 mol^{-1}): 22 in DMSO. ^{1}H-NMR spectra (δ value in ppm): δ(N–H), 8.18 (brs, 1H), δ(Ar–H), 7.02–7.46 (m, 4H); δ(CH_3), 3.56 (s, 6H), 3.48 (s, 6H), 3.32 (s, 6H). ^{13}C{^{1}H}-NMR spectra: (δ value in ppm): δ(Ar–C), 138.40(s), 125.70(s), 112.43(s); δ(S-C), 57.20(s), 54.36(s).

2. 1. 2. Synthesis of [*trans*-$RuCl_2$ $(DMSO)_3$ (btz)], Complex (2)

(a) The starting complex *trans*-$RuCl_2(DMSO)_4$ was prepared according to the method cited in literature.[17]

(b) Recrystallized *trans*-$RuCl_2(DMSO)_4$, (0.060 g, 0.12 mmol) was dissolved in 20 mL acetone. To this solution 1, 2, 3-benzotriazole (0.028 g, 0.22 mmol) dissolved in 10 mL acetone was added and the reaction mixture was kept under stirring for 6 h. A yellow precipitate appears, which was washed several times with acetone: diethyl ether: methanol (1:2:1), (v/v) solvent mixture and dried. Yield: 0.042 g (66.6%), M.p. >225 °C; Found: C, 27.40; H, 4.40; N, 8.12; S, 18.35; $C_{12}H_{23}N_3O_3S_3Cl_2Ru$ (Mτ = 525). Require(s): C, 27.42; H, 4.38; N, 8.00; S, 18.28. Selected infrared absorptions (KBr, cm^{-1}): ν(N-H), 3445(br); ν(Ru–S), 400(m); ν(SO), 1099(s), 1063(m); ν(N=N), 1420(s); ν(Ru-Cl), 340(s), 338(s); ν(Ru-N), 275(m). Electronic spectra (λmax, nm (ε in M^{-1} cm^{-1})) in acetonitrile: 680(28), 446(86), 380(908), 328(1106), 229(1440); Δm at 25 °C (Ω^{-1} cm^2 mol^{-1}): 25 in DMSO. ^{1}H-NMR spectra (δ value in ppm): δ(Ar-H), 7.07–7.58 (m, 4H); δ(N–H), 7.99 (brs, 1H); δ(CH_3), 3.52 (s, 6H); 3.36 (s, 12H). ^{13}C{^{1}H}-NMR spectra (δ value in ppm): δ(Ar-C), 137.46(s), 126.40(s), 111.31(s); δ(S-C), 54.38(s), 57.25(s).

2. 1. 3. Synthesis of $[H(btz)]^+$[*trans*-$RuCl_4$ $(DMSO)(btz)]^-$, Complex (3)

(a) The starting complex $[H(DMSO)_2]^+$ [*trans*–$RuCl_4$ $(DMSO)_2]^-$ was prepared by the method reported in literature.[18]

(b) $[H(DMSO)_2]^+$[*trans*-$RuCl_4$ $(DMSO)_2]^-$, (0.100 g, 0.17 mmol) was dissolved in 20 mL acetone and benzotriazole (0.040 g, 0.33 mmol) dissolved in ~5 mL of acetone was added to this reaction mixture. A brown orange sticky precipitate was observed after stirring for 6 h, which was washed several times with acetone: diethylether: acetonitrile (1:2:3), (v/v) solvent mixture to remove the sticky nature. Yield: 0.088 g (92.4%), M.p. >225 °C. Found: C, 29.98; H, 3.04; N, 15.04; S, 5.68. $C_{14}H_{17}N_6OSCl_4Ru$ (Mτ =560) Require(s): C, 30.01; H, 3.06; N, 15.00; S, 5.72. Selected infrared absorption: ν(N-H), 3450(m), 3435(m); ν(N=N), 1415(s); ν(SO), 1107(s), 1068(s); $[(btz)H]^+$, 752(br); ν(Ru-Cl), 340(s), 335(sh); ν(Ru-N), 280(s). Electronic Spectra (λmax, nm (ε in M^{-1} cm^{-1})) in methanol, 650(30), 476(706), 430 (989), 300(706). μ_{eff} = 1.86 μβ. Δm at 25 °C (Ω^{-1} cm^2 mol^{-1}): 120 in DMSO.

2. 1. 4. Synthesis of Na^+[*trans*-$RuCl_4$(DMSO) (btz)]$^-$, Complex (4).

(a) The starting complex Na^+[*trans*–$RuCl_4(DMSO)_2]^-$ was prepared by the method reported in literature.[18]

(b) Recrystallized Na^+[*trans*-$RuCl_4(DMSO)_2]^-$, (0.080 g, 0.18 mmol) was dissolved in 20 mL of acetone. Benzotriazole (0.045 g, 0.33 mmol) was dissolved in minimum amount of acetone (5 mL) and added to the reaction mixture. It was then kept under stirring for 7 h under inert atmosphere. The reaction mixture turned orange brown colour and a precipitate was obtained, which was washed several times with acetone: diethyl

ether: acetonitrile (1:2:1), (v/v) solvent mixture to remove sticky nature and dried in vacuum. Yield: 0.067g, (80%), M.p. >225 °C. Found: C, 20.72; H, 2.30; N, 9.02; S, 6.96. $C_8H_{11}N_3OSCl_4RuNa$ (Mτ = 462). Require(s): C, 20.77; H, 2.38; N, 9.09; S, 6.92. Selected Infrared absorptions (KBr, cm^{-1}): ν(N-H), 3455(m), 3432(m); ν (N=N), 1418(s); ν(SO), 1109(s); ν(Ru-S), 400(m); ν(Ru-Cl), 334(s), 330(sh); ν(Ru-N), 270(m). Electronic Spectra (λmax, nm (ε in M^{-1} cm^{-1})) in acetonitrile: 636 (62), 476 (602), 436 (906), 216 (806). μ_{eff} = 1.89 μβ. Δm at 25 °C (Ω^{-1} cm^2 mol^{-1}): 117 in DMSO.

2. 1. 5. Synthesis of [*cis, fac*-$RuCl_2$ $(TMSO)_3$(btz)], Complex (5)

(a) From recrystallized [*cis,fac*-$RuCl_2(S\text{-}DMSO)_3(O\text{-}DMSO)$], cis-$RuCl_2(TMSO)_4$ was prepared using the alternative procedures proposed by Alessio *et al.* which involves DMSO/ TMSO ligand exchange.[19]

(b) Recrystallized *cis*-$RuCl_2(TMSO)_4$, (0.063 g, 0.13 mmol) was dissolved in 15 mL acetone. To this solution 1, 2, 3-benzotriazole (0.032 g, 0.2 mmol) dissolved in 15 mL of acetone and reaction mixture was kept under stirring. The dark yellow precipitate appeared after 3 h, which was then recrystallized from acetone: diethyl ether (1:1), (v/v) solvent mixture and dried in vacuum. Yield: 0.0498 g (64%). M.p. >225 °C. Found: C, 35.80; H, 4.78; N, 6.94; S, 15.90; $C_{18}H_{29}N_3O_3S_3Cl_2Ru$ (Mτ = 603). Require(s): C, 35.82; H, 4.80; N, 6.96; S, 15.92. Selected Infrared absorptions (KBr, cm^{-1}): ν(N-H), 3446(m); 3430(m); ν(SO), 1119(s); ν(N=N), 1412(s), 1461(s); ν(Ru-Cl), 326(s), 330(m); ν(Ru-S), 398(m); ν(Ru-N), 271(m). Electronic Spectra (λ max, nm(ε in M^{-1} cm^{-1})) in acetonitrile solution: 630(50), 560(281), 398(606), 320(525), 282(1108). Δm at 25 °C (Ω^{-1} cm^2 mol^{-1}): 34 in DMSO. ^{1}H–NMR spectra (δvalue in ppm): δ(Ar-H), 7.05–760 (4H); δ(N-H), 7.98 (1H); δ(S-CH_2), 4.07 (4H); 3.84 (4H); 3.68 (4H); δ(S-C-CH_2), 2.304 (12H). $^{13}C\{^1H\}$-NMR spectra (δ value in ppm): δ(Ar-C), 138.46, δ125.72, δ112.43; δ(S-C), 57.88, 56.60, 55.36; δ(S-C-C), δ27.93; δ25.43.

2. 1. 6. Synthesis of [*trans*–$RuCl_2$ $(TMSO)_3$ (btz)], Complex (6)

(a) [*trans*–$RuCl_2$ $(TMSO)_4$] was prepared according to literature cited.[19]

(b) Recrystallized [*trans*-$RuCl_2(TMSO)_4$], (0.0492 g, 0.1 mmol) was dissolved in 20 mL of acetone and to this solution 1, 2, 3-benzotriazole (0.024 g, 0.20 mmol) dissolved in 20 mL of acetone was added. The dark yellow precipitate appears after 4 h, it was then concentrated under reduced pressure and then washed with acetone: diethylether (1:l) (v/v) solvent mixture and dried in vacuum. Yield: 0.0488 g (77%), M.p. >225 °C. Found: C, 35.82; H, 4.78; N, 6.90; S, 15.90; $C_{18}H_{29}N_3Cl_2S_3O_3Ru$ (Mτ = 603). Require(s): C, 35.80; H, 4.80; N, 6.96; S, 15.92. Selected Infrared absorption (KBr, cm^{-1}): ν(N-H), 3451(m); ν(N=N), 1421(s); ν(SO), 1118(s); ν(Ru-S), 402(s); ν(Ru-Cl), 326(s), 330(m); ν(Ru-N), 276(s). Electronic Spectra (λmax, nm (ε in M^{-1} cm^{-1})) in acetonitrile solution: 668(32), 460(506), 358(682), 301(703). Δm at 25 °C (Ω^{-1} cm^2 mol^{-1}): 38 in DMSO. ^{1}H-NMR spectra (δvalue in ppm): δ(N-H), 8.20 (1H); δ(Ar-H), 7.08–7.46 (4H); δ(S-CH_2), 3.36 (8H); 3.49 (4H); δ(S-C-CH_2), 3.91 (12H). $^{13}C\{^1H\}$-NMR spectra (δ value in ppm): δ(Ar-C), 137.46, δ126.40, δ112.64; δ(S-C), 54.88, 56.49; δ(S-C-CH_2), 27.72, 25.92.

2. 1. 7. Synthesis of $[H(btz)]^+$[*trans*-$RuCl_4$ $(TMSO)(btz)]^-$, Complex (7)

(a) $[H(TMSO)]^+$[*trans*-$RuCl_4(TMSO)_2]^-$ was prepared according to the method cited in literature.[19]

(b) Recrystallized $[(TMSO)H]^+$[*trans*-$RuCl_4(TMSO)_2]^-$ (0.050 g, 0.08 mmol) dissolved in 20 mL of acetone. To this solution 1, 2, 3-benzotriazole (0.020 g, 0.16 mmol) dissolved in 10 mL acetone was added. The reaction mixture was kept under stirring for more than 7 h. A yellow solution was obtained which changes into sticky precipitate on evaporation. It was washed several times with acetone and ether and recrystallized from acetone: methanol: ethanol, 3:2:1 (v/v) mixture and dried in vacuum. Yield: 0.036g (76%). M.p. >225 °C. Found: C, 32.75; H, 3.23; N, 14.34; S, 5.42. $C_{16}H_{19}SOCl_4N_6Ru$ (Mτ = 586). Require(s): C, 32.78; H, 3.27; N, 14.33; S, 5.47; Selected Infrared absorptions (KBr cm^{-1}); ν(N-H), 3451(m); ν(N=N), 1424(s); ν(SO), 1132(s); $[H(btz)]^+$, 746(br); ν(Ru-S), 402(s); ν(Ru-Cl), 326(s), 330(m); ν(Ru-N), 276(s). Electronic Spectra (λmax, nm (ε in M^{-1} cm^{-1})) in acetonitrile solution: 635(18), 465(484), 422(682), 302(702). μ_{eff} = 1.92 μβ. Δm at 25 °C (Ω^{-1} cm^2 mol^{-1}): 130 in DMSO.

3. Results and Discussions

Empirical formula of all the complexes from **1-7** is in conformity of the elemental analyses. Molar conductance of the complex **1, 2, 5** and **6** was in the range 22–38 Ω^{-1} cm^2 mol^{-1} for a very dilute solution (10^{-5} M), probably due to their non-electrolytic nature. However, molar conductance of complex **3, 4** and **7** was between 117–132 Ω^{-1} cm^2 mol^{-1} indicating their ionic nature.[17, 18]

Complex **1, 2, 5** and **6** are diamagnetic as expected for the low spin ruthenium (II) complex (low spin d^6, S = 0). All the four complexes exhibit five bands in electronic spectra. In the complex **1** and **5** first two bands observed in between 630–680 nm and 540–560 nm with a very low

extinction coefficient, may be assigned to d-d transition, $^1A_1\,g \rightarrow {}^1T_1\,g$ and $^1A_1\,g \rightarrow {}^1T_2\,g$ respectively. The bands between 380–400 nm and 320–350 nm may be attributed to MLCT transition; however the band at ~280 nm in complex **1** and **5** can easily be assigned to intraligand transition in the coordinated π – acidic imine ligand.[20, 21]

In complex **2** and **6** the two bands appeared at about 680 nm and 446 nm which can be assigned to d-d transitions, $^1A_1g \rightarrow T_1g$ and $^1A_1g \rightarrow {}^1T_2g$ respectively but the second band may have contribution from MLCT transitions. The band at about 301 nm is assigned to intra ligand transition in the coordinated π – acidic imine ligand.[20,21] Here also a band at about 229 nm is assigned for sulphoxide moiety in mixed ligand complex. Complex **3, 4,** and **7** are paramagnetic with magnetic moment 1.86–1.92 BM as evident from a low spin d^5 ruthenium (III) complex. Electronic spectra of these complexes show the band in between 630–650 nm, with a very low extinction coefficient. The bands with high optical density at about 422 nm coupled with a less intense band at λmax, 465 nm, ascribed to a charge transfer transition from chloride to Ru (III), a typical identification for $[RuCl_4]^-$ unit.[22] In complex **3** and **7** a weak absorption band at about 300 nm and 322 nm probably shows the presence of protonated cation.

FT-IR spectra of all the complexes from **1-7** show one or two bands for ν(SO) in between 1064–1118 cm^{-1}. The same band appears at 1055 cm^{-1} in free DMSO and 1023 cm^{-1} in free TMSO shows a positive shift in ν(SO) indicating the presence of S-bonded sulphoxide moiety.[23, 24] In all the complexes a new band appears at ~400 cm^{-1} assigned for ν(M-S), confirm our view. The 1, 2, 3-benzotriazole ligands contain a band at 1466 cm^{-1} for cyclic (N=N) stretching vibration. Interestingly, peak for ν(N=N) in the complexes, was observed at lower wave number (~20 cm^{-1}). This observation may be taken as evidence for coordination of one of the nitrogen of the two cyclic (N=N). The band observed for ν(M-N) at about 280 cm^{-1} is in agreement of our view. A very broad band centered at ~742 cm^{-1} observed in complex **3** and **7** along with a band for ν(SO) in free DMSO/TMSO region attributed to the presence of hydrogen bonded azolium cation. All the complexes show one or two band at ~330 cm^{-1} assigned for ν(Ru-Cl).

All the diamagnetic complex **1, 2, 5** and **6** were characterized on the basis of ^{1}H-NMR and $^{13}C\{^1H\}$-NMR spectra. In complex **1** we observed three singlets at δ3.56 ppm, δ3.48 ppm and δ3.32 ppm. The two sets of singlet at δ3.56 ppm and δ3.48 ppm for 6 protons were assigned for methyl group of DMSO situated trans to Cl probably due to their diastereotropic nature, and signal at δ3.32 ppm for 6 proton was assigned for methyl group of DMSO situated trans to 1, 2, 3,-benzotriazole unit.[16,25–27] The $^{13}C\{^1H\}$-NMR of this complex shows three signals for methyl carbon of DMSO. The signals at δ57.2 ppm and δ56.3 ppm were assigned to methyl carbon of DMSO trans to Cl and signal at δ54.36 ppm was assigned to methyl carbon of DMSO trans to 1, 2, 3-benzotriazole unit.

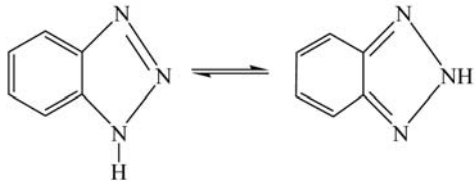
In complex **5**, the TMSO analogue we observed four sets of singlet at tmso δ2.30 ppm, δ3.68 ppm, δ 3.84 ppm and δ4.07 ppm. The signals at δ4.07 and δ3.84 ppm for 8 protons was assigned for S-CH_2 proton of the TMSO ligand trans to Cl atom, because two equivalent TMSO ligand trans to Cl are diastereotropic while signals at δ3.68 ppm for 4 protons was assigned for the S-CH_2 proton of the TMSO ligand trans to 1, 2, 3-benzotriazole. The signal at δ2.30 ppm for 12 protons was assigned for the S-C-CH_2 proton of all the three TMSO ligands.[28–33] The $^{13}C\{^1H\}$-NMR of complex **5** shows five signals. The signal at δ55.36 ppm was assigned to the (S-CH_2) carbon of the TMSO trans to 1, 2, 3-benzotriazole. The signal at δ57.88 ppm and δ56.60 ppm was assigned to the (S-CH_2) carbon trans to Cl atom. The same conclusion can be drawn for the signal observed at δ27.93 ppm and δ25.43 ppm, which were assigned for (S-C-CH_2) methylenic carbon of TMSO.

In complex **2** the DMSO analogue two sets of singlets centered at δ3.36 ppm and δ3.52 ppm were observed which corresponds to S-bonded DMSO. The relative intensity of the two is 2:1 suggested that two DMSO are trans to each other and other is trans to 1, 2, 3-benzotriazole ligand.[16, 25–27] The $^{13}C\{^1H\}$-NMR of this complex shows two signals for methyl carbon of DMSO at δ57.250 and δ54.382 ppm. The signal at δ57.25 ppm was assigned for the methyl carbon of DMSO trans to 1, 2, 3-benzotriazole and the signal at δ54.38 ppm for the methyl carbon of DMSO trans to each other.

In complex **6**, the TMSO analogue we observed three set of signals centered at δ3.91 ppm, δ3.49 ppm and δ3.36 ppm. The signal at δ3.91 ppm for eight protons was assigned for S-CH_2 proton of TMSO situated trans to each other, and the signal at δ3.49 ppm for four protons was assigned for S-CH_2 proton of TMSO situated trans to 1, 2, 3-benzotriazole ligand. The signal centered at δ3.36 ppm for 12 protons was assigned for the S-C-CH_2 proton of all the TMSO.[28–33]

$^{13}C\{^1H\}$-NMR of complex **6** shows four signals for methylenic carbon of TMSO. The signal at δ54.88 ppm was assigned for (S-CH_2) carbon of the TMSO trans to each other and the other signal at δ56.49 ppm was assigned for the TMSO trans to benzotriazole unit. Same conclusion can be inferred for the signal observed at δ27.72 ppm and δ25.92 ppm, which were assigned for (S-C-CH_2) methylenic carbon of TMSO.

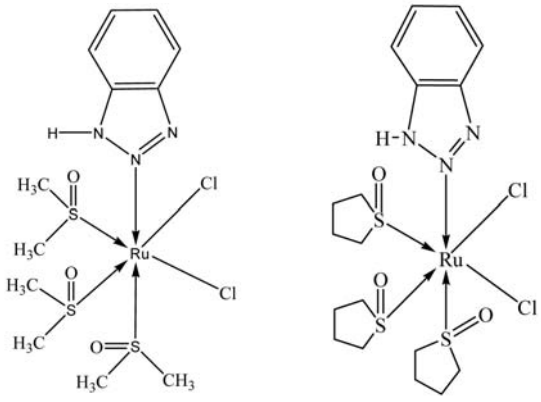
Benzotriazole exists in two tautomeric forms (A) and (B) but since 1-H tautomer (structure A) is most stable in solid state and solution we expect coordination from the 1-H tautomer. It is an aromatic ligand exhibiting three vicinal nitrogen atom available for coordination but since signal for δ(NH) in almost at the same position as it was obtained in ligand, the coordination from NH is omitted.



a) b)

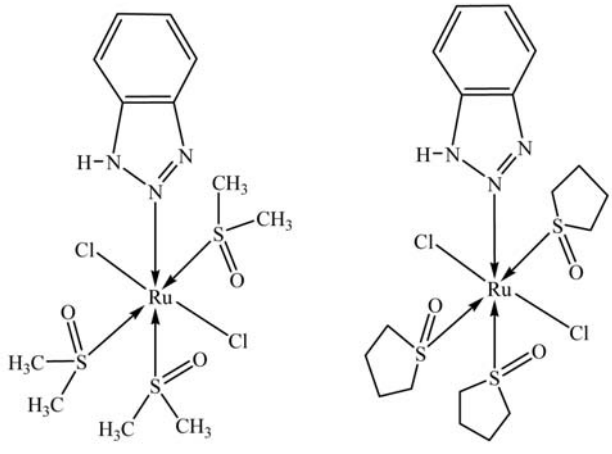
Fig. 1. Tautomeric form of 1, 2, 3-benzotriazole.

In the $^{13}C\{^1H\}$-NMR spectra of ligand, three signals observed at δ136.43 ppm, δ119.38 ppm and δ112.43 ppm were assigned for the aromatic carbon. Interestingly, these peaks are almost at the same position in the complexes. Since N(2) site becomes more competitive in case of metal ion with a single back bonding capacity we suggest coordination from N(2) site to the metal centre and the most plausible structure for the complex **1, 2, 5**, and **6** are as given in Fig 2 and Fig 3.[32,33]



Complex-1 Complex-5.

Fig. 2. Structure of complex **1** and **5**.

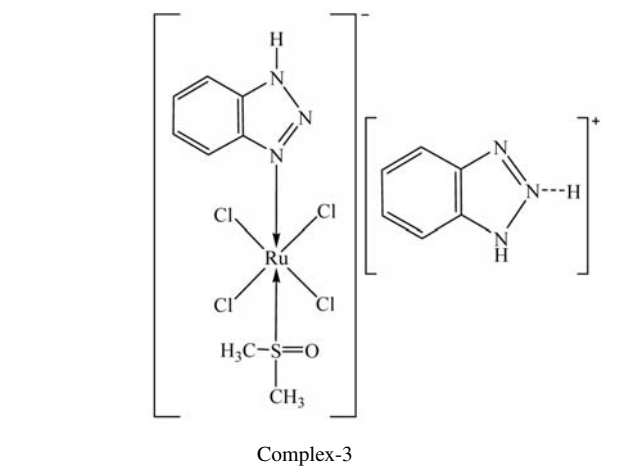


Complex-2 Complex-6

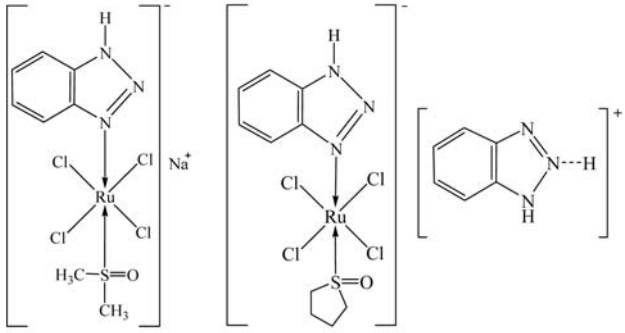
Fig. 3. Structure of complex **2** and **6**.

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

The signal in NMR spectra of the complexes **3, 4** and **7** were too broad and severely shifted from original position, due to intervention of paramagnetic ion and we are not able to use NMR as diagnostic tool in these complexes. Since N(1) is more nucleophillic than N(2), than in the complexes **3, 4, 7** we suggest coordination from this preferred site.[32,33] Thus on the basis of FT-IR, UV-VIS and elemental analysis we suggest most probable structure for the complex **3, 4** and **7** in Fig 4.



Complex-3



Complex-4 Complex-7

Fig. 4. Structure of complex **3, 4** and **7**.

4. Antibacterial Activity

Antibacterial activity of the 1, 2, 3-benzotriazole ligand and complexes **1-7** and their precursors have been tested on ***Escherichia coli***, MTCC 1304, a gram-negative bacteria at different concentrations and compared with an antibiotic Chloramphenicol. Mueller Hinton Agar plates (MHA) were prepared and 50 μL suspensions of ***Escherichia coli*** containing approximately 10^5 CFU (Colony Forming Unit) were applied to the plate by the spread plate technique.[34] The wells of 6 mm size were made on the plates and they were filled with 50 μL of sample solution

of 0.02%, 0.03% and 0.04% concentrations. Now these plates were incubated at 37±1 °C for 24–48 h in refrigerated incubator shakers. The result shows that inhibition zone was observed in all the plates of different concentration. All the complexes show positive activity against the ***E. coli*** and their diameter of inhibition zone were more than that of precursors and ligand, probably due to enhanced liphophilicity of the complexes which leads to breakdown of permeability barriers of the cell and thus retard the normal cell process in bacteria.[35, 36] The complex **3** and **4** were found very much potent in comparison to other complexes. The detail results of antibacterial activity are given in **Table 1**.

Table 1: Antibacterial activity against *Escherichia coli*

Complex/Precursor	Activity against *E. coli*	* Diameter of inhibition zone (in mm)
[*cis*-$RuCl_2(DMSO)_3$(btz)]	+	11.0
[*cis*-$RuCl_2$ $DMSO)_4$]	–	7.0
[*trans*-$RuCl_2(DMSO)_3$(btz)]	+	11.0
[*trans*-$RuCl_2(DMSO)_4$]	–	7.0
[H (btz)][*trans*-$RuCl_4$(DMSO)(btz)]	+	33.0
[H $(DMSO)_2$][*trans*-$RuCl_4(DMSO)_2$]	+	17.0
[Na][*trans*-$RuCl_4$ (DMSO) (btz)]	+	31.0
[Na][*trans*–$RuCl_4$ $(DMSO)_2$]	+	13.0
[*cis*-$RuCl_2$ $(TMSO)_3$ (btz)]	+	21.0
[*cis*-$RuCl_2$ $(TMSO)_4$]	–	7.0
[*trans*-$RuCl_2(TMSO)_3$(btz)]	+	20.0
[*trans*-$RuCl_2(TMSO)_4$]	–	6.0
[H(btz)][*trans* – $RuCl_4$(TMSO) (btz)]	+	23.0
[H $(TMSO)_2$][*trans* – $RuCl_4(TMSO)_2$]	+	9.0
1, 2, 3- Benzotriazole	+	8.0
Chloramphenicol	+	40.0

* Diameter of inhibition zone >8 mm is taken as active and shown as + in the table

5. Conclusion

We have prepared seven complexes of ruthenium(II)/ruthenium(III) dimethysulphoxide/tetramethylenesulphoxide with 1, 2, 3-benzotriazole. In complexes **1, 2, 5** and **6** one O-bonded sulphoxide moiety is replaced by incoming benzotriazole ligand linked through N(2). However, in complexes **3, 4** and **7** one S-bonded sulphoxide moiety is replaced by benzotriazole ligand linked through N(1). These complexes are novel and require further biological screening at lower dilutions. They may find more importance in future due to their other aspects of biological activity. Their characterization, reactivity and inherent activity may throw a new light on ruthenium (II) and ruthenium (III) based pharmaceuticals.

6. References

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Povzetek

Opisana je sinteza in karakterizacija sedmih rutenijevih (II) in rutenijevih (III) kloro sulfoksidnih kompleksov z 1,2,3-benzotriazolom. Možne so tri oblike produktov: : [cis,fac–$RuCl_2(so)_3(btz)$]; [trans–$RuCl_2(so)_3(btz)$] in [trans–$RuCl_4(so)(btz)]^-[X]^+$; kjer je so=dimetilsulfoksid/ tetrametilensulfoksid; btz = 1, 2, 3-benzotriazol in $[X]^+$ = $[(btz)H]^+$ ali Na^+. Kompleksi so bili okarakterizirani z elementno analizo, merjenjem prevodnosti, magnetne susceptibilnosti, FT-IR, ^{1}H-NMR, $^{13}C\{^1H\}$-NMR in elektronsko spektroskopijo. Preverjena je bila njihova protibakterijska aktivnost proti gram negativni bakteriji *Escherichia coli.* Protibakterijska aktivnost izoliranih spojin je višja kot pri ligandu 1,2,3-benzotriazolu in rutenijevih prekurzorjih. Podana je primerjava aktivnosti teh spojin glede na referenčni antibiotik kloramfenikol.