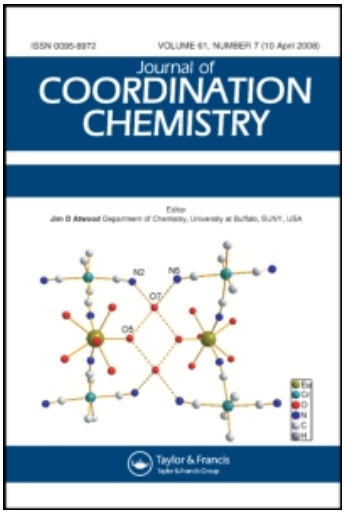

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Synthesis, spectroscopic characterization and antibacterial studies of some derivatives of chlorodimethylsulphoxide/tetramethylenesulphoxide ruthenium(II) and ruthenium(III) with 4-aminoantipyrine

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Synthesis, spectroscopic characterization and antibacterial studies of some derivatives of chlorodimethylsulphoxide/ tetramethylenesulphoxide ruthenium(II) and ruthenium(III) with 4-aminoantipyrine

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We report the synthesis of five complexes of three different formulations viz. [*cis*-$RuCl_2(4\text{-antp})_2$], [*trans*-$RuCl_2(4\text{-antp})_2$] and $[X]^+[trans\text{-}RuCl_4(4\text{-antp})_2]^-$ ($X^+ = [(DMSO)_2H]^+$, Na^+, or $[(TMSO)H]^+$ and 4-antp = 4-aminoantipyrine) from different routes. These complexes were characterized on the basis of elemental analyses, molar conductance measurements, magnetic susceptibility, electronic spectra, FTIR, ^{1}H-NMR and $^{13}C\{^1H\}$-NMR spectroscopy. Complexes were screened for antibacterial activity and found to be potent against gram negative bacteria *Escherichia coli*.

Keywords: Dimethylsulphoxide; Tetramethylenesulphoxide; Ruthenium; Antipyrine

1. Introduction

Recent research in ruthenium chemistry opens new horizons in metallopharmaceutical chemistry [1–4], supramolecular structures as electronic and photomolecular devices [5–8], intercalative properties with DNA [9] *in vitro* and as a versatile catalyst [10].

Some ruthenium compounds have good antimetastatic properties and one, NAMI-A, has successfully completed **p**hase-I and **p**hase-II trials [11]. A second ruthenium complex, indazolium [tetracholrobis (indazole) Ru^{III}], has entered clinical trials and is active against colon carcinoma and metastasis, which is a major reason for cancer mortality with no satisfactory chemotherapy [12, 13].

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¶This paper is dedicated to my teacher, Dr. H. Singh, Ex. Professor, D.D.U. University, Gorakhpur, UP, India.

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Encouraged from previous results with 2-aminobenzimidazole and 2-aminobenzothiazole [14, 15], we have taken 4-aminoantipyrine as a ligand. Antipyrine or phenazole has a pyrazolone nucleus, which is a five-member lactam ring containing two nitrogens and a ketone in the same molecule, and well known for its great pharmacological activity. Pyrazolone is useful for pharmacological ingredients especially to the class of non-steroidal anti-inflammatory agents (NSAID) used in the treatment of arthritis, other musculoskeletal joint disorders and ear preparations [16]. Therefore, we examine the reaction of ruthenium chloro sulphoxide complexes with biologically-active, bidentate, 4-aminoantipyrine, characterize the products spectroscopically and screen them for biological activity in order to establish a structure-activity relationship.

2. Experimental

$RuCl_3 \exists 3H_2O$ (E.Merck) and 4-aminoantipyrine (Lancaster, UK) were used as received. Analytical grade dimethylsulphoxide (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 on a Nicolet Magna-750 FTIR spectrophotometer. ^{1}H-NMR and $^{13}C\{^1H\}$-NMR spectra were recorded in $CDCl_3$ on a Bruker-400 MHz spectrometer. Guoy's method was employed for measurement of magnetic susceptibility. Cobalt mercury tetrathiocyanate was used as a standard. Diamagnetic corrections were made using Pascal's constants.

2.1. *Synthesis of complexes*

2.1.1. Synthesis of (1), [cis-$RuCl_2$(4-antp)$_2$]. This complex was obtained from two different routes.

(a) *Cis*-$RuCl_2(DMSO)_4$ was prepared according to the procedure cited [17]. The recrystallized *cis*-$RuCl_2(DMSO)_4$, (0.100 g, 0.2 mmol) and 4-aminoantipyrine (0.100 g, 0.49 mmol) were heated in ethanol under reflux for 18 h in an inert atmosphere. The reaction mixture was reduced to half volume by passing N_2(g). The resulting orange brown precipitate was further purified by column chromatography using silica gel (60–120 mesh). Eluting the column with 1 : 1, v/v, acetone-methanol isolated the desired product. Evaporation of solvent from the eluate yielded an orange brown solid. Yield: 0.081 g (73%), m.p. > 220°C.

(b) *Cis*-$RuCl_2(TMSO)_4$ was prepared according to the procedure cited [18], which involves a DMSO/TMSO ligand exchange. The recrystallized *cis*-$RuCl_2(TMSO)_4$ (0.100 g, 0.17 mmol) and 4-aminoantipyrine (0.090 g, 0.44 mmol) were heated in ethanol under reflux for 15 h in an inert atmosphere. Volatiles were evaporated and the solid extracted with acetone. The resulting orange brown precipitate was further purified by column chromatography. Two bands appeared in the column

and the red band was eluted with 1 : 1, v/v, diethyl ether and diethyl acetate. This separated fraction was dried in vacuum and a red product was obtained in a very small amount (0.005 g, 4.5% approximately) which readily decomposed into a black brown precipitate. Another dark brown band was eluted from 1 : 1, v/v, acetone–methanol mixture. Evaporation of the solvent from eluate yielded an orange brown solid. Yield: 0.075 g (75%), m.p. > 220°C. Found: C, 45.62; H, 4.39; N, 14.2; $C_{22}H_{26}N_6O_2Cl_2Ru$ ($M_\tau = 578$). Calcd: C, 45.67; H, 4.49; N, 14.53. Electronic spectra (λ_{max}, nm (€ in $M^{-1}\,cm^{-1}$)) in acetonitrile: 650(20), 552(32), 371(760), 320(550), 265(1109). ΔM at 25°C ($\Omega^{-1}\,cm^{-2}\,mol^{-1}$): 48 in acetone. Selected IR absorption (KBr, cm^{-1}): ν(Ru–Cl), 332(s); ν(Ru–N), 278(s); ν(N–H), 3464(m); ν(C=O), 1647(s); ν(M–O), 595(m). ^{1}H-NMR (δ in ppm): $\delta(NH_2)$, 5.14(brs, 2H), 4.98(brs, 2H); δ(Ar-H), 7.06-8.22 (m, 10H); $\delta(C–CH_3)$, 3.25(s, 6H); $\delta(N–CH_3)$, 2.63(s, 6H). $^{13}C\{^1H\}$ NMR spectra (δ in ppm): $\delta(N–CH_3)$, 79.63(s); $\delta(C–CH_3)$, 69.9(s); $\delta(N–C_6H_5)$, 122.3–128.6(m); δ(C=0), 165.6(s), 162.4(s); δ(C-4), 41.0(s); δ(C-3), 35.6(s).

2.1.2. Synthesis of (2), [*trans*-$RuCl_2$(4-antp)$_2$]. This complex was also obtained from two different routes.

(a) *Trans*-$RuCl_2(DMSO)_4$ was prepared according to the procedure cited in the literature. Recrystallized *trans*-$RuCl_2(DMSO)_4$ [1] (0.200 g, 0.41 mmol) was refluxed with 4-aminoantipyrine (0.209 g, 1.03 mmol) in ethanol for 12–13 h under inert atmosphere. Evaporation gave a brown precipitate which was recrystallized from acetone–ethanol (2 : 1 v/v) and dried in vacuum. Yield: 0.15 g (65%), m.p. > 220°C.

(b) Recrystallized *trans*-$RuCl_2(TMSO)_4$ [18] (0.100 g, 0.17 mmol) was dissolved in 20 mL of ethanol with mild stirring and 4-aminoantipyrine (0.090 g, 0.44 mmol) dissolved in minimum ethanol (~10 mL) was added. The solution was refluxed for 8–10 h in ethanol in an inert atmosphere and reduced to half volume by passing N_2(g) over hot liquid. The brown precipitate obtained was filtered, recrystallized from acetone–ethanol (2 : 1 v/v) and dried in vacuum. Yield: 0.82 g (83%), m.p. > 220°C. Found: C, 45.62; H, 4.41; N, 14.48; $C_{26}H_{26}N_6O_2Cl_2Ru$, ($M_\tau = 578$). Calcd: C, 45.67; H, 4.49; N, 14.53. Electronic spectra (λ_{max}, nm (€ in $M^{-1}\,cm^{-1}$) in acetonitrile: 475(250), 665(25), 340(853), 301(723). ΔM at 25°C ($\Omega^{-1}\,cm^{-2}\,mol^{-1}$), 40 in acetone, 68 in DMSO. Selected IR absorptions (KBr, cm^{-1}): ν(Ru–Cl), 330(s), 328(sh); ν(Ru–N), 270(s); ν(N–H), 3465; ν(C=O), 1652(s); ν(M–O), 592(m). ^{1}H-NMR (δ in ppm): $\delta(NH_2)$, 5.35(brs, 4H); (Ar-H), 7.29-8.35(m, 10H); $\delta(C–CH_3)$, 3.10(s, 6H); $\delta(N–CH_3)$, 2.89(s, 6H). $^{13}C\{^1H\}$ NMR (δ in ppm): $\delta(N–CH_3)$, 74.6(s); $\delta(C–CH_3)$, 70.2(s); $\delta(N–C_6H_5)$, 126.3–130.6(m); δ(C=0), 164.6(s); δ(C-4), 39.0; δ(C-3), 31.0.

2.1.3. Synthesis of (3), $[H(DMSO)_2]^+$[*trans*-$RuCl_4$(4-antp)]$^-$. The red crystal of $[H(DMSO)_2]^+[trans\text{-}RuCl_4(DMSO)_2]^-$ [2] (0.100 g, 0.17 mmol) was dissolved in 20 mL of methanol in a two neck flask with mild stirring. The 4-aminoantipyrine (0.0450 g, 0.22 mmol) dissolved in minimum methanol (~10 mL) in a beaker was added to the above solution and refluxed for 20 h under inert atmosphere. The reaction mixture was evaporated and reduced to half volume by passing N_2(g) over hot liquid.

The brown black precipitate obtained was washed with 1 : 1, ethanol–diethylether, recrystallized from 1 : 1, acetone–methanol and dried in vacuum. Yield: 0.82 g (75%), m.p. > 220°C. Found: C, 29.55; H, 4.03; N, 6.85; S, 10.52; $C_{15}H_{25}N_3S_2O_3Cl_4Ru$ ($M_\tau = 602$). Calcd: C, 29.90; H, 4.15; N, 6.98; S, 10.69. Electronic spectra (λ_{max} (€ in $M^{-1}\,cm^{-1}$)) in acetonitrile: 478(705), 355(900), 302(803). $\mu_{eff} = 1.89\,\mu B$, ΔM at 25°C ($\Omega^{-1}\,cm^{-2}\,mol^{-1}$), 109 in H_2O, 68 in DMSO. Selected IR absorptions (KBr, cm^{-1}): ν(Ru–Cl), 338(s), 333(sh); ν(Ru–N), 280(s); ν(N–H), 3442(m); ν(C=O), 1648(s); ν(M–O), 590(m); ν((DMSO)$_2$H), 720(br); ν(so), 1055(s).

2.1.4. Synthesis of (4), Na^+[*trans*-$RuCl_4$(4-antp)]$^-$. Recrystallized light orange crystals of Na[*trans*-$RuCl_4(DMSO)_2$] [2] (0.100 g, 0.23 mmol) was dissolved in 20 mL of methanol and 4-aminoantipyrine (0.0420 g, 0.20 mmol) dissolved in 10 mL of methanol was added and refluxed for 18 h under inert atmosphere. The initial red changes into dark brown solution and a dark brown complex obtained on vacuum evaporation was recrystallized from acetone–methanol (3 : 2 v/v) mixture. Yield: 0.068 g (37%), m.p. > 220°C. Found: C, 28.12; H, 2.73; N, 8.77. $C_{11}H_{13}N_3OCl_4RuNa$ ($M_\tau = 468$). Calcd: C, 28.20; H, 2.77; N, 8.97. Electronic spectra (λ_{max}, nm (€ in $M^{-1}\,cm^{-1}$)) in acetonitrile: 479(700), 368(783), 306(806). $\mu_{eff} = 1.87\,\mu B$. ΔM at 25°C ($\Omega^{-1}\,cm^{-2}\,mol^{-1}$), 115 in H_2O, 98 in DMSO. Selected IR absorptions (KBr, cm^{-1}): ν(Ru–Cl), 332(s), 326(sh); ν(Ru–N), 288(s); ν(N–H), 3440(m); ν(C=O), 1652(s); ν(M–O), 586(m).

2.1.5. Synthesis of (5), [(TMSO)H]$^+$[*trans*-$RuCl_4$(4-antp)]$^-$. Recrystallized [(TMSO)H] [*trans*-$RuCl_4(TMSO)_2$] [18] (0.100 g, 0.17 mmol) was dissolved in 25 mL of methanol. The 4-aminoantipyrine (0.045 g, 0.22 mmol) was dissolved in 5 mL of HCl and then added to the above reaction mixture and refluxed for 16 h under inert atmosphere. The initial purple solution changes to dark brown precipitate on vacuum evaporation, which was recrystallized from a 3 : 2 : 1, acetone–methanol–ethanol mixture. Yield: 0.058 g (42%), m.p. > 220°C. Found: C, 32.60; H, 3.94; N, 7.60; S, 5.50. $C_{15}H_{22}N_3SO_2Cl_4Ru$ ($M_\tau = 551$). Calcd: C, 32.66; H, 3.99; N, 7.62; S, 5.80. Electronic spectra (λ_{max}, nm (€ in $M^{-1}\,cm^{-1}$)) in acetonitrile: 486(450), 388(608), 336(755). $\mu_{eff} = 1.91\,\mu B$, ΔM at 25°C ($\Omega^{-1}\,cm^{-2}\,mol^{-1}$), 120 in H_2O, 106 in DMSO. Selected IR absorptions (KBr, cm^{-1}): ν(Ru–Cl), 328(s); ν(Ru–N), 275(s); ν(N–H), 3444(m); ν(C=O), 1648(s); ν(M–O), 570(m); ν((TMSO)H$^+$, 705(br); $\nu(so)_{str}$, 1025(s).

3. Results and discussion

Stoichiometries of all complexes from **1**–**5** are in conformity of the elemental analysis. Molecular conductances of **1** and **2** were initially low for a very dilute (10^{-3} M) aqueous solution but increase slowly to that for a 1 : 1 electrolyte on keeping the solution for 6–8 h. Molar conductances of **3**, **4** and **5** were initially that of a 1 : 1 electrolyte, indicating their ionic nature [1, 17].

3.1. *Complexes 1 and 2*

Complexes **1** and **2** are diamagnetic as expected for low-spin ruthenium(II) (low spin, d_6, S=O). Complex **1** has five bands in the electronic spectra at 650 nm, 552 nm, 371 nm, 320 nm and 265 nm. The weak bands at 650 nm and 552 nm may be assigned to d–d transitions, $^1A_1g \rightarrow {}^1T_1g$ and $^1A_1g \rightarrow {}^1T_2g$, respectively, and the band at 371 nm can be assigned to MLCT transitions. The bands at 320 nm and 265 nm with higher extinction coefficients are intraligand transitions. Similarly, **2** shows three bands in electronic spectra. The bands at 645 nm and 475 nm can be assigned to d–d transitions, $^1A_1g \rightarrow {}^1T_1g$ and $^1A_1g \rightarrow {}^1T_2g$, respectively, but may be due to MLCT, especially the band at lower frequency with high extinction coefficient. The bands at 340 nm and 301 nm can easily be assigned to intraligand transitions [19–22].

FTIR spectra of ligand display a sharp peak at 1680 cm^{-1} for ν(C=O) and a broad peak at 3502 cm^{-1} for (N–H) stretching vibration. However, in the complex both signals were shifted downward ($\sim$35 cm^{-1}), indicating coordination of ligand through the nitrogen of $-NH_2$ group and O of C=O group. This was also confirmed by the appearance of a ν(Ru–N) peak around 275 cm^{-1} and ν(Ru–O) peak at about 595 cm^{-1}. A sharp band observed around 330 cm^{-1} was assigned to ν(Ru–Cl) stretching mode.

The band observed for coordinated DMSO/TMSO between 1090-1130 cm^{-1} for ν_{so} and around 400 cm^{-1} for $\nu_{M\text{-}S}$ in the precursor complexes, *cis*/*trans*-$RuCl_2(SO)_4$, where SO = DMSO/TMSO, completely disappeared in **1** and **2**, indicating total displacement of sulphoxide in these complexes [23–25].

^{1}H-NMR spectra of **1** show two broad singlets at δ 5.14 ppm and δ 4.98 ppm (2 protons) which were assigned for NH_2 *trans* to Cl and NH_2 *trans* to CO. A multiplet was observed between δ 7.06–8.25 ppm for 10H of the two aromatic benzene rings and singlets at δ 3.25 ppm and δ 2.63 ppm, each for 6 protons (expected for methyl group linked to C-3 carbon and methyl linked to N).

$^{13}C\{^1H\}$ NMR spectra display two signals at δ 165.6 ppm and δ 162.4 ppm assigned for C=O *trans* to Cl and to NH_2 group. These signals were upfield shifted from the signal observed for C=O (δ 170.3 ppm) in the ligand indicating C=O coordination to the metal. We observed one singlet centered at δ 79.3 ppm and another at δ 69.9 ppm, assigned for methyl carbon of CH_3–N and CH_3–C-3 carbon. A multiplet for aromatic carbon between δ 122.3–128.6 ppm was observed. Two signals observed at δ 41.0 ppm and δ 35.6 ppm were expected for C-4 and C-3, respectively.

^{1}H-NMR of **2** has one broad singlet centered at δ 5.35 ppm for 4H, expected for the two NH_2 groups situated *trans* to CO, a multiplet between δ 7.29–8.35 observed for 10 aromatic protons and two singlets centered at δ 3.10 ppm and δ 2.891 ppm, expected for methyl linked to C_3 and CH_3 linked to N.

$^{13}C\{^1H\}$ NMR spectra show a singlet at δ 164.6 ppm for C=O bonded to the metal, singlets at δ 74.6 ppm (for methyl carbon of CH_3-N) and at δ 70.2 ppm (for methyl carbon of CH_3–C-3), a multiplet for aromatic carbon between δ 126.3–130.6 ppm, two signals at δ 39.0 ppm and δ 31.0 ppm for C-4 and C-3 carbons, respectively. Thus, on the basis of UV-Vis, FTIR, ^{1}H-NMR and $^{13}C\{^1H\}$ NMR we suggest structures for **1** and **2** (figure 1).

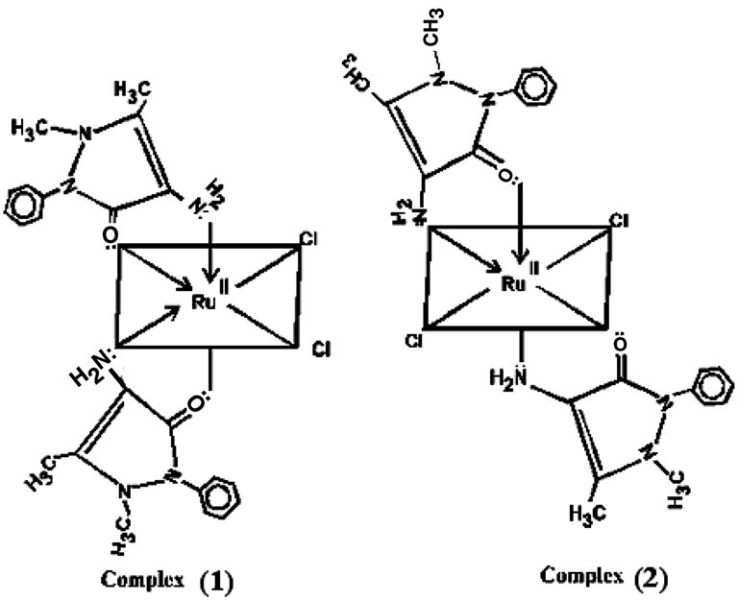

Figure 1. Complexes **1** and **2**.

3.2. *Complexes 3, 4 and 5*

Complexes **3**, **4** and **5** were paramagnetic with magnetic moments of 1.89 μβ, 1.87 μβ and 1.91 μβ, respectively, at room temperature, lower than the normal value (2.10 μβ). The low μ_{eff} value may be due to the presence of low symmetry ligand fields, metal-metal interactions and extended overlap of metal and ligand orbitals [26]. The magnetic moments of complexes with T_{2g} ground term are lowered due to progressive quenching of the orbital angular momentum by spin orbital coupling, which removes the degeneracy of the triplet ground term. Extensive spin orbit coupling can reduce the moment below the spin only value.

All three complexes show three bands in electronic spectra. The first and second bands, between 478–486 nm and 355–388 nm, can be assigned to MLCT transitions and the third observed between 302–332 nm to intraligand transition [20–23].

FTIR spectra of complexes **3**, **4** and **5** show shifts of ν(C=O) and ν(N–H) lower, indicating coordination through amino-N and carbonyl-O. These data were supplemented by appearance of ν(M–N) and ν(M–O) peaks around 280 cm^{-1} and 580 cm^{-1}. The spectra of these complexes display a sharp peak at 330 cm^{-1} for ν(Ru–Cl). FTIR spectra of **3**, **4** and **5** reveal the absence of coordinated DMSO/TMSO due to disappearance of absorptions in the region 1090–1130 cm^{-1} for coordinated sulphoxide ν(S=O) and around 400 cm^{-1} for ν(M–S). The presence of ν(SO) for free sulphoxide (DMSO/TMSO) at 1055 cm^{-1} for **3** and at 1025 cm^{-1} for **5**, along with a characteristic broad O···H···O stretching band at 700 cm^{-1}, indicates the presence of $[H(DMSO)_2]^+$ and $[H(TMSO)]^+$ cations [27].

Interference of paramagnetic ion signals in ^{1}H-NMR and $^{13}C\{^1H\}$ NMR spectra of complexes **3**, **4** and **5** prevented us from using NMR as a diagnostic tool, but on the basis of FTIR, UV-Vis, elemental analysis and molar conductance, we suggest the structure for these complexes (figure 2).

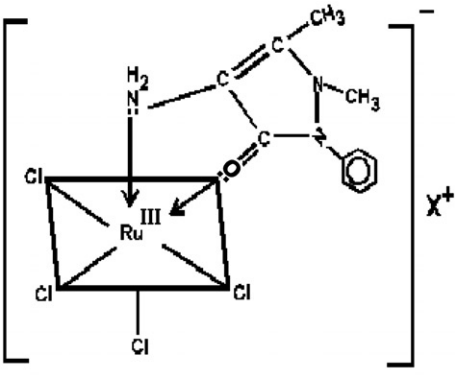

Figure 2. Suggested structure for complexes **3**, **4** and **5**.

Reaction of *cis*-$RuCl_2(SO)_4$/*trans*-$RuCl_2(SO)_4$ with 4-aminoantipyrine ligand in 1 : 2 molar ratio replaced all the sulphoxides in the coordination sphere and lead to the same product, whether DMSO or TMSO existed in the starting complex. For $[H(SO)_n][$*trans*-$RuCl_4$(4-antp)], where SO = DMSO/TMSO and $n = 2/1$, the sulphoxides in the coordination sphere were replaced with 4-aminoantipyrine but the sulphoxide present as a hydrogen bonded unit in the outer coordination sphere were not replaced.

3.3. *Antibacterial activity*

(a) Antibacterial experiment

Antibacterial activity of **A** (A = 4-aminoantipyrine), complexes **1**–**5** and their precursors **1a**–**5a** and **1b**–**2b** have been tested on *Escherichia coli*, MTCC 1304, a gram negative bacteria at different concentration. Muller Hinton Agar (MHA) plates 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 [28]. The wells made on the plate were filled with 50 μL of sample solution of 0.03% concentration and the plates were incubated at 37±1°C for 24–48 h in a refrigerated incubator shaker.

(b) Results

No inhibition zone was observed around the controls, **A** and complex **1** (table 1). Complex **1** shows no inhibition zone even at 0.04% and 0.05% concentration. However, complexes **2**, **3**, **4** and **5** show more inhibition than their precursors **2a/b, 3a**–**5a**, probably due to their increased lipophilicity in the complexes [29, 30]. Complex **4** was found most active than all other complexes at this particular concentration.

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

S.No.	Compound/Precursor	Activity against *Escherichia coli*	Inhibition zone diameter (in mm)
1	[*cis*-$RuCl_2$(4-antp)$_2$], (Compound-1)	−	8
1a.	[*cis*-$RuCl_2$(DMSO)$_4$]	−	7
1b.	[*cis*-$RuCl_2$(TMSO)$_2$]	−	8
2	[*trans*-$RuCl_2$(4-antp)$_2$], (Compound-2)	+	15
2a.	[*trans*-$RuCl_2$(DMSO)$_4$]	−	7
2b.	[*trans*-$RuCl_2$(TMSO)$_4$]	−	8
3	[H(DMSO)$_2$] [(*trans*-$RuCl_4$(4-antp)],	+	25
3a.	(Compound-3)	+	19
	[H(DMSO)$_2$] [(*trans*-$RuCl_4$(DMSO)$_2$]		
4	Na[*trans*-$RuCl_4$(4-antp)],	+	30
4a.	(Compound-4)	+	12
	Na[*trans*-$RuCl_4$(DMSO)$_2$]		
5	[H(TMSO)] [(*trans*-$RuCl_4$(4-antp)],	+	22
5a.	(Compound-5)	+	9
	[H(TMSO)] [(*trans*-$RuCl_4$(TMSO)$_2$]		
6	4-Aminoantipyrine (Compound–A)	−	8

Zone diameter of inhibition > 8 mm is taken as active and shown as + in the table.

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