SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND ANTIBACTERIAL ACTIVITY OF SOME CHLOROSULPHOXIDE RUTHENIUM (II) AND RUTHENIUM (III) COMPLEXES OF 4-(BENZYLIDENEAMINO)-1,2-DIMETHYL-2-PHENYL-1,2-DIHYDROPYRAZOLE-3-ONE, SCHIFF BASE

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ABSTRACT

In present work we report the synthesis of five complexes of three different formulations, viz. [cis-$RuCl_2(SBANTP)_2$]; [trans-$RuCl_2(SBANTP)_2$]; and $[RuCl_4(SBANTP)^-][X]^+$; where $[X]^+$ = $[(dmso)_2H]^+$, Na^+ or $[(tmso)H]^+$ and SBANTP = 4-(benzyideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydropyrazole-3-one, from different routes. The complexes were characterized on the basis of elemental analyses, molar conductance measurements, magnetic susceptibility, electronic spectra, FTIR, ^{1}H-NMR,^{13}C{^{1}H}NMR spectroscopy, FAB-Mass spectrometry. Complex **2** was also analyzed by EDX analysis.The 3D molecular modeling and analysis for bond length and bond angle have been also carried out for one of the representative complex 1. All the five complexes were screened for antibacterial activity and found to be more potent against gram negative bacteria *Escherichia coli* than their precursors but less active than chloramphenicol.

Keywords: Dimethylsulphoxide, Tetramethylenesulphoxide, Ruthenium, Schiff base, Antipyrine.

INTRODUCTION

The chemistry of ruthenium (II)/(III) sulphoxide pave a new way to various fields of research, i.e., metallopharmaceuticals[1-3] supramolecular electronic and photomolecular devices,[4-6] intercalative properties with DNA *in vitro*[7] and as a versatile catalyst.[8]

The imidazolium salt, NAMI-A has completed phase-I and phase-II trials,[9] and the ruthenium (III) indazole salt, KP1019 has also entered in phase-I trial and found active against colon carcinoma and their metastasis.[10-11]

The syntheses of half-sandwich ruthenium (II) complexes with new N, S-donor Schiff base ligands have developed considerable interest in Schiff base ruthenium derivative.[12] Antimicrobial studies of ruthenium complexes containing Schiff base have been reported.[13] Some Schiff base complexes have also been reported to show good antibacterial activity.[14-15]

Encouraged from previous experience with 2-aminobenzimidazole, 2-aminobenzothiazole and especially with 4-aminoantipyrine, we have taken here Schiff base of 4-aminoantipyrine as a ligand.[16-18] Pyrazolone is a 5-membered lactam ring derived from pyrazole, which has a keto group. It is well known for its great pharmacological activity and anti-inflammatory property.[19]

Therefore, it will be of interest for us to see the reaction of ruthenium chlorosulphoxide complexes with biologically active bidentate Schiff base,4-(benzylideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydropyrazole-3-one (SBANTP) and to characterize it spectroscopically. Although some studies have been performed on biological activity of ruthenium sulphoxide complexes, the quest for the development of new bioactive molecule still persist, and hence we have checked antibacterial activity of the compounds synthesized.

EXPERIMENTAL

$RuCl_3.3H_2O$ (E. Merck), 4-aminoantipyrine, tetramethylene sulphoxide (Lancaster, UK), benzaldehyde (BDH) were used as received. Analytical grade dimethyl sulphoxide (BDH) and solvents were used without further purification for synthetic purposes. Electronic absorption spectra were recorded with shimadzu-1700, UV-VIS spectrophotometer equipped with a PC**.** Conductivity measurements were carried out at 25ºC on an EI-181 conductivity bridge with a dipping type cell**.** FTIR spectra were recorded in KBr pellets on shimadzu-8400 PC, FTIR spectrophotometer. ^{1}H-NMR and ^{13}C{^{1}H} NMR spectra were recorded in DMSO-d_6 on a Bruker Avance-400 NMR spectrometer. Guoy`s method was employed for measurement of magnetic susceptibility. Cobalt mercurytetrathiocyanate was used as standard. Diamagnetic correction was made using Pascal's constant. Elemental analyses (C, H, N) were performed on Elementra Vario EL- III, Elemental analyzer. EDX analysis was carried out on Genesis-2000**.** FAB-Mass spectra of complexes were recorded on Jeol SX-102 mass spectrometer.

Synthesis of 4-(benzyideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazole-3-one,Schiff base[20]

The 4-aminoantipyrene (0.406g, 2.0mmol) was dissolved into 20ml of ethanol in a flask with mild stirring. Few drop of glacial acietic acid was added which works as catalyst. Benzaldehyde (0.20ml, 2.0mmol) was added into the above reaction mixture with the help of a micropipette and resulting solution was refluxed for 10-12h at 70-80^{0}C. Thereafter, reaction mixture was cooled to room temperature, concentrated and poured into crushed ice with constant stirring. A yellow-orange precipitate was obtained, which was filtered, washed with sodiumbisulphite, vacuum dried and recrystallized from methanol-ethanol-acetone, 3:2:1 (v/v) mixture. Yield: 0.466g (80.0%). Found: C, 74.01; H, 5.80; N, 14.38; $C_{18}H_{17}N_3O$ (M_1 = 291). Required: C, 74.21; H, 5.88; N, 14.42. Selected IR absorption (KBr, cm^{-1}): ν(N-CH_3)str, 3160; $n_{C=O,}$ 1644(s); ν(CH=N), 1595(s). ^{1}H-NMR (δ value in ppm): d(CH=N), 9.76 (S,1H); δ(Ar-H), 7.38-7.68(m,10H); δ(N-CH_3), 3.46(S,3H); δ(CH_3), 2.64 (S,3H). ^{13}C{^{1}H}NMR (d value in ppm) : δ(C=O), 176.3; δ(CH=N), 155.0, δ(Ar-C), 120.8-129.4; d(N-CH_3), 82.4; δ(CH_3), 71.4; δ(C-4), 42.6; δ(C-5), 35.6.

Synthesis of complexes

Synthesis of [cis-$RuCl_2(SBANTP)_2$]; Complex 1 :

[Cis,fac-$RuCl_2(S\text{-}dmso)_3(O\text{-}dmso)$] was prepared according to procedure cited in literature.[21] The recrystallized [cis,fac-$RuCl_2(S\text{-}dmso)_3(O\text{-}dmso)$], (0.070g, 0.14mmol) and SBANTP (0.084g, 0.28mmol) were stirred in acetone for 8h. The reaction mixture was evaporated and reduced to half by passing a flux of N_2 gas. The dark brown precipitate was further purified by column chromatography. Eluting the column isolated the desired product by a 1:1, v/v, methanol-acetone mixture. Evaporation of solvent from the eluate yielded a light brown solid. Yield: 0.035g(33%); M.p. > 220ºC.

Cis-$RuCl_2(tmso)_4$ was prepared according to procedure cited in literature which involve a dmso/tmso ligand exchange.[23] The recrystallized [cis-$RuCl_2(tmso)_4$], (0.070g, 0.11mmol) was dissolved in 20ml methanol and SBANTP (0.070g, 0.24mmol), were added and stirred for 7h in an inert atmosphere. The reaction mixture was vacuum evaporated. The resulting light brown precipitate was further purified by column chromatography using silica gel (50-120 mesh) eluting the column isolated the desired product by a 1:1 v/v, methanol-acetone mixture. Evaporation of the solvent from eluate yielded a dark brown solid. Yield: 0.044g (53%), M.p. > 220ºC, Found: C, 57.20; N, 4.48; N, 11.38; $C_{36}H_{34}N_6O_2Cl_2Ru$, (M_1=754), requires: C, 57.30; H, 4.51; N, 11.44. Selected IR absorption (KBr, cm^{-1}): ν(C=O), 1624(s); ν(CH=N), 1568(s); ν(M-O), 550(s); ν(Ru-Cl), 330(s); ν(Ru-N), 278(s). Electronic spectra (λ_{max}, nm (E in M^{-1} cm^{-1})) in acetonitrile: 630(30); 560(45); 380(602); 326(826).

^{1}H-NMR (d value in ppm): δ(CH=N), 10.25(S,1H), 10.08(S,1H);δ(Ar-H), 7.05-8.25(m, 20H); δ(N-CH_3), 3.30 (S,6H), d(C-CH_3), 2.61, (S,6H). $^{13}C\{^1H\}$ NMR spectra (d value in ppm) : δ(C=O), 172.02(s), 169.84(s); δ(CH=N), 162.32(s) 160.20(s),;δ(Ar-C),121.24-128.33; δ(N-CH_3), 82.63(s); δ(C-CH_3), 70.02(s); δ(C-4), 41.03(s); δ(C-5), 34.08(s); FAB-Mass: $[MH]^+$,755.

Synthesis of [trans-$RuCl_2(SBANTP)_2$]; Complex 2 :

Two different routes obtained this complex:

trans-$RuCl_2(dmso)_4$ was prepared according to procedure cited in literature.[22] The recrystallized [trans-$RuCl_2(dmso)_4$], (0.040g, 0.08mmol) was stirred with Schiff base, SBANTP (0.048g, 0.16mmol) in acetone for 8h under an inert atmosphere. On evaporation of solution, light orange crystal was obtained which was filtered and recrystallized from ethanol:acetone (2:1) v/v mixture. Yield: 0.035g (57%).

trans-$RuCl_2(tmso)_4$ was prepared according to the reported method,[23] The recrystallized [trans-$RuCl_2(tmso)_4$], (0.040g, 0.06mmol) was dissolved in acetone with mild stirring. The SBANTP (0.040g, 0.13mmol) was dissolved in acetone and added to the above solution. After 7h stirring under an inert atmosphere, light brown precipitate obtained which was filtered and recrystallized from ethanol: acetone (2:1), v/v mixture. Yield: 0.0286g (57%), M.p. > 220ºC, Found: C, 57.26; H, 4.32; N, 11.03; $C_{36}H_{34}N_6O_2Cl_2Ru$ (M_t=754), requires: C, 57.31; H, 4.51; N, 11.44. Selected IR absorption (KBr, cm^{-1}): ν(C=O), 1614(s); ν(CH=N), 1565(s); n(M-O), 550(s); n(Ru-N), 272(s); n(Ru-Cl),328(s). Electronic spectra ($\lambda_{max,}$ nm (E in M^{-1} cm^{-1})) in acetonitrile: 660(22), 486(300); 348(786), 308(633). Dm at 25ºC (Ω^{-1} cm^{-2} mol^{-1}), 36 in dmso. ^{1}H-NMR spectra (d value in ppm): δ(CH=N), 10.48 (S, 2H), δ(Ar-H), 7.20-8.48(m, 20H); d(N-CH_3), 3.44 (S, 6H); δ(C-CH_3), 2.58 (S, 6H). $^{13}C\{^1H\}$ NMR spectra (δ value in ppm): δ(C=O), 170.70(s); δ(CH=N), 162.68(s); δ(Ar-C), 126.78-129.73(m); δ(N-CH_3), 79.60(s); δ(C-CH_3), 70.20(s); δ(C-4), 39.88(s); δ(C-3), 31.84(s); FAB-Mass ;$[MH]^+$,755.

Synthesis of $[H(dmso)_2]^+$ $[RuCl_4(SBANTP)]^-$, Complex 3 :

The complex $[H(dmso)_2]^+$[trans-$RuCl_4(dmso)_2]^-$ was prepared according to the procedure cited in literature.[21] The crystals of $[H(dmso)_2]^+$[trans-$RuCl_4(dmso)_2]^-$ (0.140g, 0.29mmol) was dissolved in 10 ml of acetone with mild stirring under inert atmosphere. The SBANTP (0.087g, 0.30mmol) was dissolved in acetone in a beaker and added to the above solution and stirred for 6h. The reaction mixture was evaporated to half of its volume by passing flux of N_2 gas. The brown colour precipitate was obtained, which was filtered and recrystallized from 1:1 ethanol: acetone mixture and dried in vacuum. Yield: 0.078 (46%), M.p. > 220ºC, Found: C, 39.05; H, 4.35; N, 6.18; S, 9.26. $C_{22}H_{30}N_3S_2O_3Cl_4Ru$ (M_t= 691), requires C, 38.21; N, 4.37; N, 6.08, S, 9.27. Selected IR absorption (KBr, cm^1): ν(C=O), 1619(s); ν(CH=N), 1562 (s); ν(n_{SO}),1049 ; ν$[(dmso)_2H]^+$, 771.4(br); ν(M-O), 550(s); ν(Ru-Cl), 332(s), 330(sh); ν(Ru-N), 272(s); Electronic spectra ($l_{max,}$ nm (Î in $M^{-1}cm^{-1}$)) in acetonitrile: 475(680), 422(1020), 352(860), 300(981). m_{eff} = 1.87 m_B. Dm at 25ºC (W^{-1} cm^{-2} mol^{-1}): 140 in dmso. FAB-Mass; $[MH]^+$, 692.

Synthesis of Na^+ $[RuCl_4(SBANTP)]^-$, Complex 4 :

The complex Na^+ [trans-$RuCl_4(dmso)_2]^-$ was prepared according to procedure cited in literature.[21] The recrystallized orange crystal of Na^+ [trans-$RuCl_4(dmso)_2]^-$, (0.030g, 0.072mmol) was dissolved in 10ml of acetone. The SBANTP (0.021g, 0.072mmol) was dissolved in 10ml of acetone and added to the above solution and the solution was stirred for 8h under inert atmosphere. The dark brown solution was obtained. A light brown complex was obtained on evaporation, which was filtered and recrystallized from ethanol: acetone, 3:2 v/v, mixture. Yield: 0.0148g (37.5%), M.p. > 220ºC, Found, C, 38.62; H, 2.98; N, 7.48; $C_{18}H_{17}N_3Cl_4RuNa$ (M_t = 557), requires, C, 38.78; H, 3.05; N, 7.54. Selected IR absorption (KBr, cm^{-1}): ν(C=O), 1619(s); ν(CH=N), 1560(s) ν(M-O), 550(s); ν(Ru-Cl), 330(s), 326(sh); ν(Ru-N), 280(s). Electronic spectra (l_{max}, **nm** (in M^{-1}, cm^{-1})) in acetonitrile: 486(692); 430(980); 355(740); 302(880). m_{eff} = 1.89m_B.FAB-Mass; [M Na]$^+$,580.

Synthesis of $[RuCl_4(SBANTP)][(tmso)H^+]$, Complex 5 :

The complex [trans-$RuCl_4(tmso)_2]^-$ $[(tmso)H]^+$ was prepared according to procedure cited in literature.[22] The crystal of [trans-$RuCl_4(tmso)_2$][(tmso) H]$^+$, (0.140g, 0.25mmol) was dissolved in 10 ml of acetone with mild stirring. The SBANTP (0.077g, 0.26mmol) was dissolved in acetone in a beaker and added to the above solution. The reaction mixture was evaporated to half of its volume. The dark brown colour precipitate was obtained, which was filtered and recrystallized from 1:1, ethanol: acetone mixture. Yield: 0.074g (46%), M.p.> 220ºC. Found: C, 41.25; H, 4.01; N, 6.50; $C_{22}H_{26}N_3O_2SRuCl_4$ (M_t=639), requires: C, 41.31; H, 4.07; N, 6.57. Selected IR absorption (KBr,cm^{-1}): ν(C=O),1616(s); ν(CH=N),1566(s); ν(M-O),545(s); ν(Ru-Cl), 328(s),322(sh); n(Ru-N), 284(s). Electronic spectra (λ_{max}, nm (Î in $M^{-1}cm^{-1}$)) in acetonitrile: 492(340); 428(868); 382(620); 326(860). μ_{eff} = 1.94m_B.Dm at 25ºC (Ω^{-1} cm^{-2} mol^{-1}), 142 in dmso. FAB-Mass; $[MH]^+$, 640.

RESULTS AND DISCUSSION

Stoichiometries of all the complexes from **1**-**5** are in conformity of the elemental analysis. FAB-mass spectra shows pseudomolecular ion peak for the complexes, which was also in agreement with molecular formula. Molecular conductance of the complex **1** and **2** were initially low for a very dilute (10^{-3} m) aqueous solution but increase slowly on keeping the solution for 6-8h to that for a 1:1 electrolyte. However, molar conductance of the complex **3**, **4** and **5** were initially high to that 1:1 electrolyte indicating their ionic nature.[22]

Complex 1 and 2

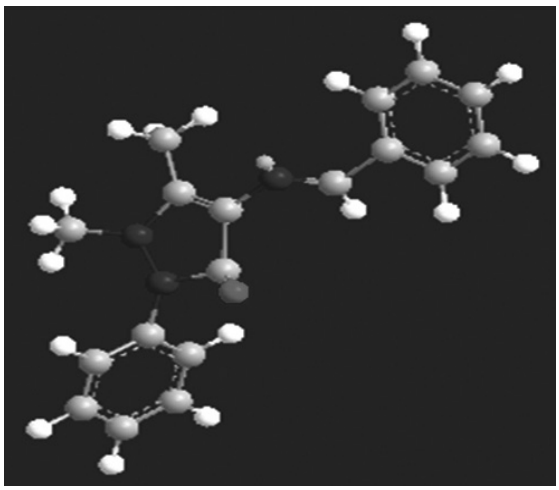
Complex **1** and **2** are diamagnetic as expected for the low spin ruthenium (II) complexes (low spin, d^6, S=O). Complex **1** shows four bands in electronic spectra. The weak bands at 630nm and 560nm, may be assigned to d-d transition $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ respectively, and the third band at 380nm with high extinction coefficient can easily be assigned to MLCT transitions.[23-26] The band at 326nm is assigned as intraligand transition. Similarly, complex **2** shows four bands in electronic spectra. The bands at 660nm and 486nm can be assigned to d-d transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{2g} \rightarrow {}^1T_{2g}$ respectively, but it may have contribution from MLCT transition especially the band at lower frequency with high extinction coefficient. The bands at 348nm and 308nm may be attributed to MLCT and intraligand transitions respectively.[23-26]

FTIR spectra of ligand displays a sharp peak at about 1644cm^{-1} for n(C=O) stretching vibration. In complexes this peak was shifted downwards (~30cm^{-1}) indicating coordination of oxygen of C=O to ruthenium metal center. This was further supported by appearance of a peak for ν(M-O) at about 550cm^{-1} in the far IR region.

Similarly the peak observed at 1595cm^{-1} in ligand attributed for ν(CH=N) shifted downwards (~30cm^{-1}) in the complexes, was an affirmative indication for coordination of azomethine nitrogen to ruthenium metal center. This was also supported by appearance of a band in far IR region at about 270cm^{-1} assigned for n(M-N). A sharp band observed around 300cm^{-1} was assigned to ν(Ru-Cl) stretching mode. Interestingly, it was observed that the entire band observed for coordinated dmso/tmso in between 1067-1115cm^{-1} for n_{SO} and around 424cm^{-1} for n_{M-S} in the precursor complexes, cis/trans $RuCl_2(SO)_4$, where SO = dmso/tmso, completely disappeared in the complex **1** and **2**. This was an indication of the total displacement of sulphoxide moiety from these complexes.[27-29]

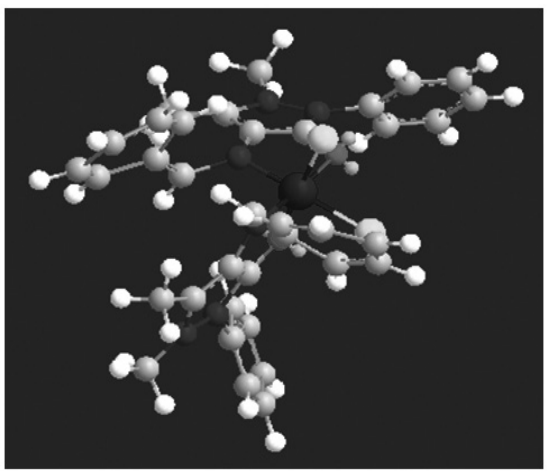
^{1}H-NMR of ligand displays a signal at δ 9.76ppm assigned for azomethine (CH=N) which was downfield shifted in both **1** and **2**, confirming coordination through azomethine nitrogen. Interestingly, it splits and appeared at d 10.25ppm and d 10.08ppm in complex **1**, which was probably due to (CH=N) situated trans to Cl and (CH=N) situated trans to O. In complex **2**, its signal was observed at d 10.48ppm for 2H, probably due to azomethine group situated in same environment. We observed a multiplet between δ 7.05-8.48ppm assigned for 20H of the substituted aromatic benzene ring in both complexes. Complex **1** and **2** display two singlets at about δ 2.58ppm and d 3.92ppm each for 6 protons, which were assigned for methyl group linked to C-5 carbon and methyl linked to N.

$^{13}C\{^1H\}$ NMR spectra of complex **1** displays two signal at δ 172.02ppm and d 169.84ppm as expected for C=O trans to Cl and C=O trans to azomethine (CH=N) group. These two signals were already upfield shifted from the signal observed for C=O (δ 176.36ppm) in the ligand indicating coordination of C=O to the metal center. Thus, FTIR and $^{13}C\{^1H\}$NMR have concluded in the same direction regarding CO coordination**.** In both complexes, we have observed one singlet at δ 80.0ppm and another one at d 70.0ppm, which were assigned for methyl carbon of CH_3-N and CH_3-C-5 carbon. The signals for aromatic carbon were observed between d 121.24-129.73ppm. Two signals observed at δ 40.00ppm and d 30.00ppm were expected for C-4 and C-5 carbon respectively. Interestingly, complex **1** display two signals in $^{13}C\{^1H\}$ NMR spectra at δ 160.20ppm and δ 162.32ppm, indicating different environment around azomethine (CH=N) carbon. However, complex **2** displays only one signal at δ 162.68, assigned for two azomethine (CH=N) carbon in same environment. Thus, on the basis of UV-VIS, FTIR, ^{1}H-NMR, $^{13}C\{^1H\}$NMR, and FAB-Mass spectra we suggest the following structure as most plausible structure for complex **1** and **2**.

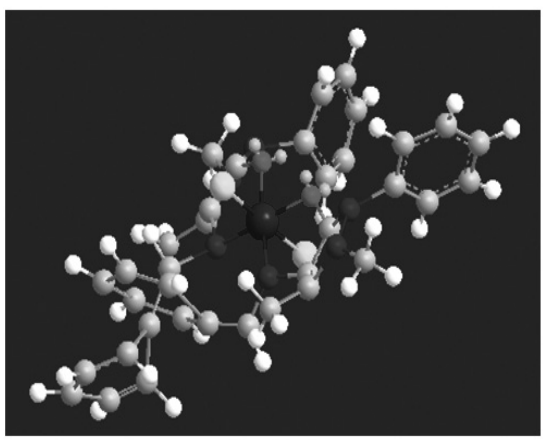


Ligand: 4-(benzyideneamino)-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazole-3-one, (SBANTP).

Fig. 1



Complex 1



Complex 2

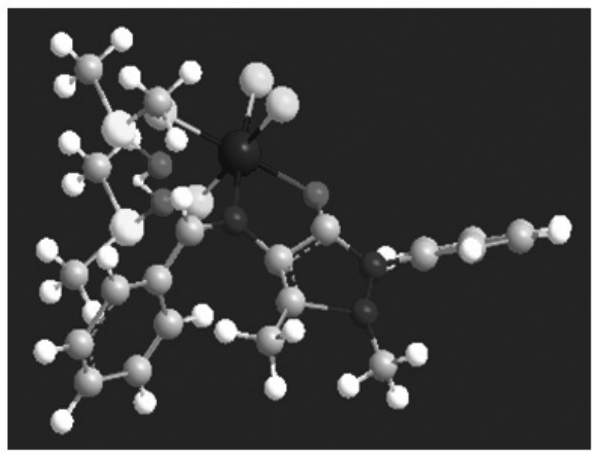
Fig. 2

Complex 3, 4 and 5

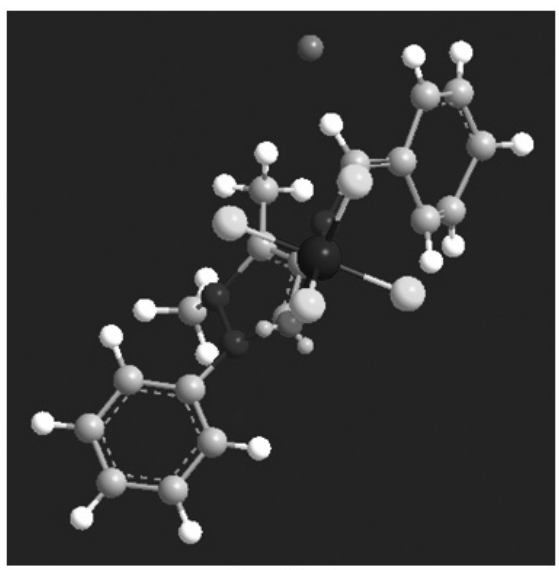
Complex **3**, **4** and **5** were paramagnetic with magnetic moment 1.87-1.90 m_B. These values are quite lower than the normal value (2.10 μ_B). This low m_{eff} value may be due to combination of factors including the presence of low symmetric ligand fields, metal-metal interactions and the formation of molecular orbital by extended overlap of metal ligand orbital.[30-31] All the three complexes show four bands in electronic spectra. The first two bands were assigned to MLCT transitions and second and third bands with high extinction were assigned for intraligand transition.[23-25] The band with high optical density ~420nm coupled with a less intense band ~486nm was ascribed to charge transfer from chloride to Ru(III).[26]

FTIR spectra of complex **3**, **4** and **5** also display the shifting of υ(C=O) and u(CH=N) vibration to the lower one, indicating the coordination of ligand through azomethine-**N** and carbonyl-O to the ruthenium metal center. Here, also the above data were supplemented by appearance of υ(M-N) and υ(M-O) peaks around 270cm^{-1} and 550cm^{-1}. The spectra of these complexes displays a peak for υ(Ru-Cl) at around 330cm^{-1}. Interestingly, FTIR spectra of **3**, **4** and **5** also reveals the absence of coordinated dmso/tmso, due to complete disappearance of peak in the region 1099-1179cm^{-1} for coordinated sulphoxide υ(S=O) and around 400cm^{-1} for u(M-S). But obviously, the presence of υ(SO) for free sulphoxide moiety (dmso/tmso) at 1049cm^{-1} for complex **3** and at 1028cm^{-1} for complex **5** along with a characteristic broad O.....H.....O stretching band centered around 771cm^{-1} indicates the presence of $[H(dmso)_2]^+$ and $[H(tmso)]^+$ cation, respectively.

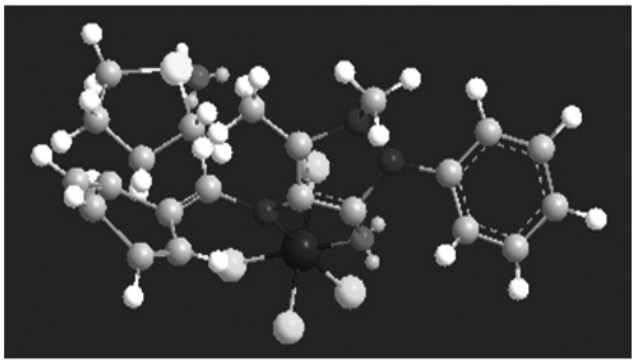
Due to interference of paramagnetic ion, signals in ^{1}H-NMR spectra and $^{13}C\{^1H\}$NMR spectra of complex **3** and **4** were too broad and shifted from original position which prevented us to use NMR as a diagnostic tool but on the basis of FTIR, UV-VIS, FAB-mass, elemental analysis and molar conductance, we suggest most probable structure for these complexes as follows:



Complex 3;



Complex 4



Complex 5.

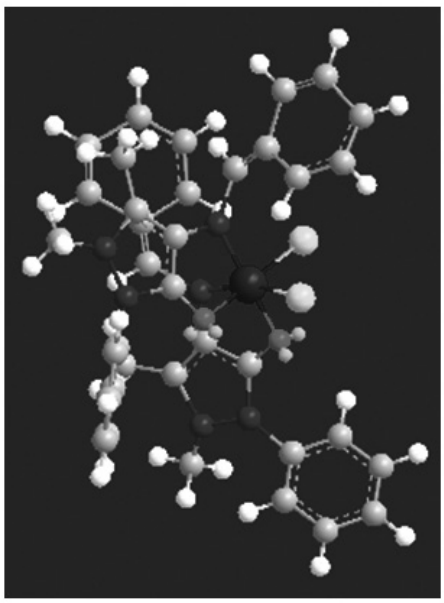
Fig. 3

EDX (Energy Dispersive X-ray) Analysis

For surface studies and microchemical analysis with elemental identification EDX analysis is used in complex **2**. The sample was analyzed *in situ*, moist, in air and without preparation or coating. Elemental distribution map shows that C and O were predominantly localized in all over the area. Ru and Cl were showing distribution having low concentration. EDX spectra shows substantial C while O, Cl and Ru appear less concentrated. Elements weight percent (%) and atomic percent (%) are given with EDX spectra.

Molecular modeling and analysis

In view of octahedral environment at ruthenium center in complex 1-5, the molecular modeling of one representative complex 1 has been carried out here. The details of bond lengths and bond angles as per 3D structure (Fig. 4) are given in the Table 1 and 2 respectively. In all 92 measurements of bond lengths and 165 measurements of bond angles are given in Table 1 and 2.



3D structure of Complex 1

Fig. 4

Table 1. Bond length of the 3D structure for complex 1.

S. No.	Atoms	Bond length	Optimal Bond length
1.	C(1)-C(2)	1.418	-
2.	C(1)-C(6)	1.419	-
3.	C(1)-H(81)	1.123	-
4.	C(2)-C(3)	1.420	-
5.	C(2)-H(79)	1.123	-
6.	C(3)-C(4)	1.419	-
7.	C(3)-H(78)	1.123	-
8.	C(4)-C(5)	1.415	-
9.	C(4)-H(77)	1.123	-
10.	C(5)-C(6)	1.419	-
11.	C(5)-H(80)	1.123	-
12.	C(6)-N(7)	1.574	-
13.	N(7)-C(8)	1.577	-
14.	N(7)-N(11)	1.510	-
15.	C(8)-C(9)	1.416	-
16.	C(8)-O(29)	1.400	-
17.	C(9)-C(10)	1.408	-
18.	C(9)-N(20)	1.549	-
19.	C(10)-N(11)	1.600	-
20.	C(10)-C(16)	1.535	-
21.	N(11)-C(12)	1.434	-
22.	C(12)-H(13)	1.122	-
23.	C(12)-H(14)	1.122	-
24.	C(12)-H(15)	1.122	-
25.	C(16)-H(17)	1.120	-
26.	C(16)-H(18)	1.122	-
27.	C(16)-H(19)	1.123	-
28.	N(20)-C(21)	1.626	-
29.	N(20)-Ru(58)	1.956	2.088
30.	C(21)-C(23)	1.319	-
31.	C(21)-H(22)	1.121	-
32.	C(23)-C(24)	1.678	-
33.	C(23)-C(28)	1.680	-
34.	C(24)-C(25)	1.368	-
35.	C(24)-H(76)	1.125	-
36.	C(25)-C(26)	1.462	-
37.	C(25)-H(74)	1.121	-
38.	C(26)-C(27)	1.676	-
39.	C(26)-H(65)	1.108	-
40.	C(27)-C(28)	1.319	-
41.	C(27)-H(64)	1.119	-
42.	C(28)-H(75)	1.121	-
43.	O(29)-Ru(58)	1.924	2.022
44.	O(29)-Lp(82)	0.649	-
45.	O(29)-Lp(83)	0.650	-
46.	C(30)-C(31)	1.446	-
47.	C(30)-C(35)	1.441	-
48.	C(30)-H(70)	1.096	-
49.	C(31)-C(32)	1.445	-
50.	C(31)-H(68)	1.096	-
51.	C(32)-C(33)	1.445	-
52.	C(32)-H(67)	1.097	-
53.	C(33)-C(34)	1.445	-
54.	C(33)-H(66)	1.096	-
55.	C(34)-C(35)	1.443	-

56.	C(34)-H(69)	1.097	-
57.	C(35)-N(36)	1.561	-
58.	N(36)-C(37)	1.567	-
59.	N(36)-N(40)	1.507	-
60.	C(37)-C(38)	1.448	-
61.	C(37)-O(57)	1.379	-
62.	C(38)-C(39)	1.465	-
63.	C(38)-N(61)	1.507	-
64.	C(39)-N(40)	1.609	-
65.	C(39)-C(45)	1.515	-
66.	N(40)-C(41)	1.434	-
67.	C(41)-H(42)	1.122	-
68.	C(41)-H(43)	1.122	-
69.	C(41)-H(44)	1.122	-
70.	C(45)-H(46)	1.122	-
71.	C(45)-H(47)	1.120	-
72.	C(45)-H(48)	1.122	-
73.	C(49)-C(51)	1.309	-
74.	C(49)-N(61)	1.630	-
75.	C(49)-H(50)	1.122	-
76.	C(51)-C(52)	1.674	-
77.	C(51)-C(56)	1.692	-
78.	C(52)-C(53)	1.442	-
79.	C(52)-H(73)	1.100	-
80.	C(53)-C(54)	1.451	-
81.	C(53)-H(71)	1.097	-
82.	C(54)-C(55)	1.684	-
83.	C(54)-H(63)	1.100	-
84.	C(55)-C(56)	1.314	-
85.	C(55)-H(62)	1.114	-
86.	C(56)-H(72)	1.116	-
87.	O(57)-Ru(58)	1.924	-
88.	O(57-Lp(84)	0.650	-
89.	O(57)-Lp(85)	0.648	-
90.	Ru(58)-Cl(59)	2.267	2.242
91.	Ru(58)-Cl(60)	2.261	2.242
92.	Ru(58)-N(61)	1.961	2.088

Table 2. Bond angle for the 3D structure of complex 1.

S. No.	Atoms	Bond Angle	Optimal Bond Angle
1.	C(2)-C(1)-C(6)	119.472	120
2.	C(2)-C(1)-H(81)	120.270	120
3.	C(6)-C(1)-H(81)	120.254	120
4.	C(1)-C(2)-C(3)	120.184	120
5.	C(1)-C(2)-H(79)	120.008	120
6.	C(3)-C(2)-H(79)	119.805	120
7.	C(2)-C(3)-C(4)	120.174	120
8.	C(2)-C(3)-H(78)	120.084	120
9.	C(4)-C(3)-H(78)	119.741	120
10.	C(3)-C(4)-C(5)	119.725	120
11.	C(3)-C(4)-H(77)	120.428	120
12.	C(5)-C(4)-H(77)	119.845	120
13.	C(4)-C(5)-C(6)	120.117	120
14.	C(4)-C(5)-H(80)	120.296	120
15.	C(6)-C(5)-H(80)	119.579	120
16.	C(1)-C(6)-C(5)	120.323	120
17.	C(1)-C(6)-N(7)	122.785	120
18.	C(5)-C(6)-N(7)	116.808	120
19.	C(6)-N(7)-C(8)	122.261	120
20.	C(6)-N(7)-N(11)	129.446	-
21.	C(8)-N(7)-N(11)	105.390	-
22.	N(7)-C(8)-C(9)	107.805	109
23.	N(7)-C(8)-O(29)	129.696	-
24.	C(9)-C(8)-O(29)	121.262	120
25.	C(8)-C(9)-C(10)	113.996	120
26.	C(8)-C(9)-N(20)	110.566	120
27.	C(10)-C(9)-N(20)	135.164	-
28.	C(9)-C(10)-N(11)	106.641	-
29.	C(9)-C(10)-C(16)	128.539	-
30.	N(11)-C(10)-C(16)	124.675	-
31.	N(7)-N(11)-C(10)	105.733	-
32.	N(7)-N(11)-C(12)	125.627	-
33.	C(10)-N(11)-C(12)	127.372	-
34.	N(11)-C(12)-H(13)	111.217	109
35.	N(11)-C(12)-H(14)	108.895	109
36.	N(11)-C(12)-H(15)	109.814	109
37.	H(13)-C(12)-H(14)	108.828	109
38.	H(13)-C(12)-H(15)	108.993	109
39.	H(14)-C(12)-H(15)	109.059	109
40.	C(10)-C(16)-H(17)	110.715	109
41.	C(10)-C(16)-H(18)	109.249	109
42.	C(10)-C(16)-H(19)	110.239	109
43.	H(17)-C(16)-H(18)	108.973	109
44.	H(17)-C(16)-H(19)	108.466	109
45.	H(18)-C(16)-H(19)	109.169	109
46.	C(9)-N(20)-C(21)	121.072	-
47.	C(9)-N(20)-Ru(58)	109.296	-
48.	C(21)-N(20)-Ru(58)	128.960	-
49.	N(20)-C(21)-C(23)	123.005	120
50.	N(20)-C(21)-H(22)	118.606	120
51.	H(22)-C(21)-C(23)	118.201	120
52.	C(21)-C(23)-C(24)	123.243	120
53.	C(21)-C(23)-C(28)	122.131	120
54.	C(24)-C(23)-C(28)	114.354	120
55.	C(23)-C(24)-C(25)	119.423	120
56.	C(23)-C(24)-H(76)	118.859	120
57.	C(25)-C(24)-H(76)	121.444	120
58.	C(24)-C(25)-C(26)	121.247	120
59.	C(24)-C(25)-H(74)	121.608	120
60.	C(26)-C(25)-H(74)	117.134	120
61.	C(25)-C(26)-C(27)	120.595	120
62.	C(25)-C(26)-H(65)	119.281	120
63.	C(27)-C(26)-H(65)	119.685	120
64.	C(26)-C(27)-C(28)	121.124	120
65.	C(26)-C(27)-H(64)	118.035	120
66.	C(28)-C(27)-H(64)	120.808	120
67.	C(23)-C(28)-C(27)	117.971	120
68.	C(23)-C(28)-H(75)	120.338	120
69.	C(27)-C(28)-H(75)	121.656	120
70.	C(8)-O(29)-Ru(58)	110.347	-
71.	C(8)-O(29)-Lp(82)	109.354	-
72.	C(8)-O(29)-Lp(83)	108.942	-
73.	Ru(58)-O(29)-Lp(82)	109.658	-
74.	Ru(58)-O(29)-Lp(83)	109.793	-
75.	Lp(82)-O(29)-Lp(83)	108.719	-

76.	C(31)-C(30)-C(35)	119.654	120
77.	C(31)-C(30)-H(70)	120.106	120
78.	C(35)-C(30)-H(70)	120.230	-
79.	C(30)-C(31)-C(32)	120.100	-
80.	C(30)-C(31)-H(68)	119.975	-
81.	C(32)-C(31)-H(68)	119.918	-
82.	C(31)-C(32)-C(33)	120.059	-
83.	C(31)-C(32)-H(67)	120.049	-
84.	C(33)-C(32)-H(67)	119.890	-
85.	C(32)-C(33)-C(34)	119.802	-
86.	C(32)-C(33)-H(66)	120.188	-
87.	C(34)-C(33)-H(66)	120.005	-
88.	C(33)-C(34)-C(35)	119.989	-
89.	C(33)-C(34)-H(69)	119.843	-
90.	C(35)-C(34)-H(69)	120.152	-
91.	C(30)-C(35)-C(34)	120.394	-
92.	C(30)-C(35)-N(36)	120.578	-
93.	C(34)-C(35)-N(36)	118.817	-
94.	C(35)-N(36)-C(37)	123.008	-
95.	C(35)-N(36)-N(40)	130.527	-
96.	C(37)-N(36)-N(40)	106.419	-
97.	N(36)-C(37)-C(38)	109.549	-
98.	N(36)-C(37)-O(57)	130.901	-
99.	C(38)-C(37)-O(57)	118.604	-
100.	C(37)-C(38)-C(39)	110.589	-
101.	C(37)-C(38)-N(61)	111.621	-
102.	C(39)-C(38)-N(61)	137.060	-
103.	C(38)-C(39)-N(40)	107.333	-
104.	C(38)-C(39)-C(45)	126.364	-
105.	N(40)-C(39)-C(45)	125.638	-
106.	N(36)-N(40)-C(39)	106.037	-
107.	N(36)-N(40)-C(41)	125.072	-
108.	C(39)-N(40)-C(41)	125.220	-
109.	N(40)-C(41)-H(42)	108.805	-
110.	N(40)-C(41)-H(43)	110.127	-
111.	N(40)-C(41)-H(44)	111.056	-
112.	H(42)-C(41)-H(43)	109.030	-
113.	H(42)-C(41)-H(44)	108.689	-
114.	H(43)-C(41)-H(44)	109.094	-
115.	C(39)-C(45)-H(46)	109.344	-
116.	C(39)-C(45)-H(47)	111.241	-
117.	C(39)-C(45)-H(48)	109.310	-
118.	H(46)-C(45)-H(47)	108.610	-
119.	H(46)-C(45)-H(48)	109.308	-
120.	H(47)-C(45)-H(48)	109.001	-
121.	C(51)-C(49)-N(61)	121.345	-
122.	H(50)-C(49)-C(51)	119.640	-
123.	H(50)-C(49)-N(61)	118.980	-
124.	C(49)-C(51)-C(52)	121.792	-
125.	C(49)-C(51)-C(56)	122.259	-
126.	C(52)-C(51)-C(56)	115.774	-
127.	C(51)-C(52)-C(53)	118.805	-
128.	C(51)-C(52)-H(73)	121.232	-
129.	C(53)-C(52)-H(73)	119.454	-
130.	C(52)-C(53)-C(54)	120.794	-
131.	C(52)-C(53)-H(71)	119.724	-
132.	C(54)-C(53)-H(71)	119.472	-
133.	C(53)-C(54)-C(55)	121.827	-
134.	C(53)-C(54)-H(63)	118.235	-
135.	C(55)-C(54)-H(63)	119.826	-
136.	C(54)-C(55)-C(56)	121.484	-
137.	C(54)-C(55)-H(62)	117.416	-
138.	C(56)-C(55)-H(62)	121.087	-
139.	C(51)-C(56)-C(55)	118.710	-
140.	C(51)-C(56)-H(72)	119.558	-
141.	C(55)-C(56)-H(72)	121.723	-
142.	C(37)-O(57)-Ru(58)	111.394	-
143.	C(37)-O(57)-Lp(84)	108.009	-
144.	C(37)-O(57)-Lp(85)	108.830	-
145.	Ru(58)-O(57)-Lp(84)	109.451	-
146.	Ru(58)-O(57)-Lp(85)	110.141	-
147.	Lp(84)-O(57)-Lp(85)	108.957	-
148.	N(20)-Ru(58)-O(29)	88.295	90
149.	N(20)-Ru(58)-O(57)	174.777	-
150.	N(20)-Ru(58)-Cl(59)	101.371	90
151.	N(20)-Ru(58)-Cl(60)	89.774	90
152.	N(20)-Ru(58)-N(61)	90.119	90
153.	O(29)-Ru(58)-O(57)	95.675	90
154.	O(29)-Ru(58)-Cl(59)	84.181	90
155.	O(29)-Ru(58)-Cl(60)	175.386	180
156.	O(29)-Ru(58)-N(61)	85.176	90
157.	O(57)-Ru(58)-Cl(59)	82.452	90
158.	O(57)-Ru(58)-Cl(60)	86.511	90
159.	O(57)-Ru(58)-N(61)	86.843	90
160.	Cl(59)-Ru(58)-Cl(60)	92.096	90
161.	Cl(59)-Ru(58)-N(61)	164.066	180
162.	Cl(60)-Ru(58)-N(61)	99.022	90
163.	C(38)-N(61)-C(49)	120.992	-
164.	C(38)-N(61)-Ru(58)	109.010	-
165.	C(49)-N(61)-Ru(58)	123.173	-

Except few case optimal values, which are more favorable of both bond length and bond angles are given along with the actual ones. The actual bond length/bond angles given in Table 1 and 2 are calculated values as a result of energy optimization in Chem 3D Ultra, while the optimal bond length/optimal bond angles are most favorable (standard) bond length/bond angles established by builder unit of Chem 3D. The missing of some values of standard bond length/bond angles may be due to limitations of software. In most of the case actual bond length and angles are closed to optimal values and thus the proposed structure of the compound is acceptable.

Antibacterial Activity

Antibacterial activity of compound A (A = SBANTP) and complex **1**, **2**, **3**, **4** and **5** alongwith their precursors **1a-5a** and **1b-2b** have been tested on *Escherichia coli*, MTCC 1304, a gram negative bacteria at different concentration.

Mullar Hinton Agar (MHA) plates were prepared at 50**µl** suspension of *Escherichia coli*, containing approximately 10^5 CFU (Colony Forming Unit) were applied to the plate by spread plate technique.[32] The wells made on the plate were filled with 50**µl** of sample solution of 0.03% concentration. Chloramphenicol solution of 0.03% was used for comparison. Now, these plates were incubated at 37±1ºC for 24-48h in a refrigerated incubator shaker. The result shows (Table 3) that very little inhibition zone was observed around the control compound **A**. However all complexes show more inhibition than their precursor, probably due to increased lipophilicity in the complexes.[33, 34] The complex **3**, **4** and **5** were found most active than all other complexes at 0.03% concentration but at the same concentration these complexes were less active than chloramphenicol, the antibiotic used for comparison.

CONCLUSION

Therefore, it can be concluded that the reaction of cis-$RuCl_2(SO)_4$/ trans-$RuCl_2(SO)_4$ with SBANTP ligand in 1:2 molar ratio replaced all the sulphoxides. We obtained same product, whether it is dmso/tmso from different

routes. But in case of $[H(SO)_n][RuCl_4(SBANTP)]$, all the sulphoxide moiety present in coordination sphere replaced with SBANTP, but sulphoxide present as hydrogen bonded unit in outer coordination sphere was not replaced, which was also confirmed by EDX. These complexes are new and may find much importance in future.

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Table 3: Antibacterial activity against Escherichia coli.5.

S. No.	Compound/Precursor	Activity against *E. coli*	Inhibition zone diameter (in mm)
1.	$[cis\text{-}RuCl_2(SBANTP)_2]$, compound **1**	+	16
1a.	$[cis\text{-}RuCl_2(dmso)_4]$	–	7
1b.	$[cis\text{-}RuCl_2(tmso)_4]$	–	7
2.	$[trans\text{-}RuCl_2(SBANTP)_2]$, compound **2**	+	22
2a.	$[trans\text{-}RuCl_2(dmso)_4]$	–	8
2b.	$[trans\text{-}RuCl_2(tmso)_4]$	–	7
3.	$[H(dmso)_2]^+[RuCl_4(SBANTP)]^-$, compound **3**	+	28
3a.	$[H(dmso)_2]^+[RuCl_4(dmso)_2]^-$	+	16
4.	$Na^+[RuCl_4(SBANTP)]^-$, compound **4**	+	32
4a.	$Na^+[RuCl_4(dmso)_2]^-$	+	11
5.	$[H(tmso)]^+[RuCl_4(SBANTP)]^-$, compound **5**	+	26
5a.	$[H(tmso)]^+[RuCl_4(tmso)_2]^-$	+	10
A.	Schiff base (SBANTP)	+	9
B.	Chloramphenicol	+	40

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