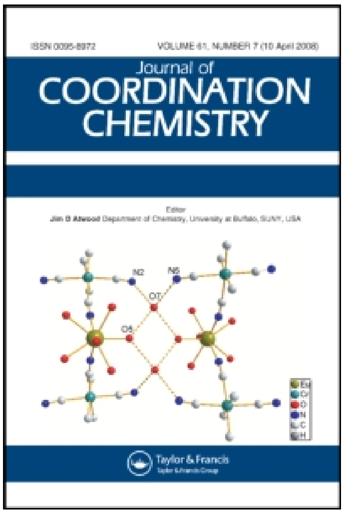

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Synthesis and spectroscopic characterization of some novel Ru(II) and Ru(III) dimeric sulphoxide complexes containing the Schiff base *N,N'*-*bis*(2-chlorobenzylidene)-1,2-ethylenediamine as spacer

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Synthesis and spectroscopic characterization of some novel Ru(II) and Ru(III) dimeric sulphoxide complexes containing the Schiff base *N*,*N′*-*bis*(2-chlorobenzylidene)-1, 2-ethylenediamine as spacer

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We report the synthesis and characterization of anionic and neutral dimers of three general formulations viz. [{*cis*-$RuCl_2(SO)_3\}_2$(2-ClBENEN)]; [{*trans*-$RuCl_2(SO)_3\}_2$(2-ClBENEN)] and $[X]_2^+[\{RuCl_4(SO)\}_2$(2-ClBENEN)$]^{2-}$; where SO = dimethylsulphoxide/tetramethylenesulphoxide; X = $[(dmso)_2H]^+$; Na^+; $[(tmso)H]^+$; and 2-ClBENEN = *N*,*N′*-*bis*(2-chlorobenzylidene)-1,2-ethylenediamine. These complexes were characterized on the basis of elemental analysis, magnetic susceptibility, electronic, FTIR, ^{1}H-NMR and $^{13}C\{^1H\}$NMR spectroscopy. These complexes are rare examples where a Schiff-base ligand serves as a spacer group.

Keywords: Ruthenium; Dimethylsulphoxide; Tetramethylenesulphoxide; Schiff base

1. Introduction

The chemistry of ruthenium(II,III)-dimethylsulphoxide and tetramethylenesulphoxide complexes has accelerated to probe their anticancer properties. Ruthenium compounds such as $[Ru(dmso)_4Cl_2]$, $[Ru(NH_3)_4Cl_2]$, ImH$[Ru(Im)_2Cl_4]$ and ImH $[Ru(Im)(dmso)Cl_4]$ (NAMI-A) are well known antitumour agents [1–7]. NAMI-A has successfully completed clinical phase-I [8]. Similarly, [IndH]$[Ru(Ind)_2Cl_4]$ has entered in clinical trials and found active against colon carcinoma and their metastasis, a major reason for cancer mortality for which no satisfactory chemotherapy exists [9]. Furthermore photochemical and electrochemical properties of ruthenium chelates with supramolecular structure have been used as electronic and photomolecular devices [10–13]. Ford *et al*. demonstrated the enhanced basicity of pyrazine when bound to Ru(II) and

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suggested the possibility of replacing the proton with another metal ion to give binuclear complex [14], relevant in further investigation of Ru(II, III) ligand back-bonding interaction [15]. Investigation of a series of Ru(III)-dmso-heterocylic *N*-donor derivatives has been carried out by Lengo *et al.* [16]. Bidentate Schiff bases are excellent chelating ligands with biological properties but are not established as bridging ligands [17, 18]. In the present investigation, we explore the reactivity of Ru–dmso/tmso species with the bidentate N-donor Schiff-base ligand *N*,*N*′-*bis*(2-chlorobenzylidene)-1,2-ethylenediamine,(2-ClBENEN) as a spacer.

2. Experimental

$RuCl_3 \cdot 3H_2O$ (E. Merck), tetramethylenesulphoxide,2-chlorobenzaldehyde (Lancaster, UK), 1,2-*bis*(ethylenediamine) (CDH) and dimethylsulphoxide (BDH) were used as received. Analytical grade solvents were used without purification for synthetic purposes. FTIR spectra were recorded on Nicolet Magna-750 FTIR spectrophotometer. Electronic absorption spectra were recorded with Systronics-2201, double beam spectrophotometer equipped with PC. Conductivity measurements were carried out at 25°C on an ELICOCM-180 Conductivity Bridge with dipping type cell. ^{1}H-NMR spectrum and $^{13}C\{^1H\}$NMR spectrum were recorded in dmso-d6 on Bruker-400 MHz spectrometer. Guoy's method was employed for measurement of magnetic susceptibility. Cobalt mercury tetrathiocyanate was used as standard with diamagnetic correction made using Pascal's constant.

2.1. *Synthesis of Schiff base:* N,N′-bis*(2-chlorobenzylidene)-1,2-ethylenediamine, (2-Cl BENEN)*

1,2-*bis* (ethylenediamine) and 2-chlorobenzaldehyde were mixed in 1 : 2 molar ratio in water and stirred for 4–5 h. A white precipitate was obtained which was recrystallized from ethanol/water, 2 : 1 (v/v) and vacuum dried. Yield 80%, m.p. > 225°C. Found: C, 62.90; H, 4.52; N, 9.12; $C_{16}H_{14}N_2Cl_2$ requires: C, 62.92; H, 4.59; N, 9.18. Selected IR absorptions: (KBr, cm^{-1}): υ(CH=N), 1640(s); υ(CH_2–CH_2), 860(m), 876(sh), ^{1}H-NMR: (400 MHz, $CDCl_3$ (δ value in ppm)): δ(Ar–H), 7.01–7.78(8H); δ(CH=N), 8.365(2H); δ(CH_2), 2.486(4H). $^{13}C\{^1H\}$NMR: δ(Ar–C), 126.20–130.68; δ(CH=N), 165.60; δ (CH_2–CH_2), 114.24.

Synthesis of complexes

2.2. *Synthesis of 1, [*{cis-*$RuCl_2(dmso)_3$}$_2$(2-ClBENEN)]*

cis-$RuCl_2(dmso)_4$ was prepared according to the method reported by Evans *et al.* [1]. The recrystallized *cis*-$RuCl_2(dmso)_4$, (0.100 g, 0.20 mmol) and the Schiff-base 2-ClBENEN (0.064 g, 0.21 mmol) were stirred for 2 h in ethanol under inert atmosphere. The colour of the reaction mixture changed from light yellow to light brown. Thereafter, *cis*-$RuCl_2(dmso)_4$ (0.100 g, 0.2 mmol) was dissolved into 10 mL of ethanol and added to above reaction mixture and refluxed for 12–15 h. The reaction mixture was reduced to half under a flow of N_2(g). The resulting dark brown black precipitate was recrystallized from a mixture of acetone/diethylether, 2 : 8 (v/v), and vacuum dried. Yield 0.145 g (65%) m.p. > 225°C. Found: C, 29.98; H, 4.32; N, 2.46; S, 17.02; $C_{28}H_{50}S_6O_6N_2Cl_6Ru_2$ ($M_\tau = 1117$) requires: C, 30.02; H, 4.47; N, 2.51; S, 17.18. Electronic spectra (λ_{max}, nm (ε in $M^{-1}cm^{-1}$)) in acetonitrile, 369(921), 326(700) 258(1008) 210 nm (868). ΔM at 25°C ($\Omega^{-1}cm^{-1}mol^{-1}$) is 46 in acetone. Selected FTIR absorptions (KBr, cm^{-1}): υ(SO), 1100(s), 1098(sh); υRu–Cl, 332(s); υCH=N, 1618(s); υ(Ru–N), 270(s); υ(Ru–S), 401(s); υ(CH_2–CH_2), 913(m), 842(m). ^{1}H-NMR spectra (δ in ppm): δ(Ar-H), 7.02–7.80(8H); δ(CH=N), 8.92(2H); δ(CH_3), 3.50(24H), 3.41(12H); δ(CH_2), 2.362(4H). $^{13}C\{^1H\}$NMR: δ(CH_3), 45.68, 44.06; δ(CH=N), 162.80; δ(Ar–C) 128.68; δ(CH_2–CH_2), 116.23; 110.42.

2.3. *Synthesis of 2, [{***trans***-$RuCl_2(dmso)_3$}$_2$2-ClBENEN]*

trans-$RuCl_2(dmso)_4$ was prepared by photoisomerization as reported by Alessio *et al.* [3]. Recrystallized *trans*-$RuCl_2(dmso)_4$, (0.100 g, 0.20 mmol) was stirred with 2-Cl BENEN (0.067 g, 0.22 mmol) for 4 h under inert atmosphere. Thereafter, 0.20 mmol *trans*-$RuCl_2(dmso)_4$, was dissolved in 10 mL of ethanol and added to the reaction mixture. The initial yellow coloured solution, which changed to light brown after 4 h, now became darker. The reaction mixture was evaporated and a black precipitate was obtained which was recrystallized from 3 : 1, acetone : diethylether, (v/v) and dried in vacuum. Yield 0.168 g (75%) m.p. > 225°C. Found: C, 30.12; H, 4.58; N, 2.61; S, 17.28; $C_{28}H_{50}S_6O_6N_2Cl_6Ru_2$ ($M_\tau = 1117$) requires: C, 30.02; H, 4.47; N, 2.51; S, 17.18. Electronic spectra (λ_{max}, nm (ε in $M^{-1}cm^{-1}$)) in acetonitrile, 450(860), 341(760), 300(660), 210(508). ΔM at 25°C ($\Omega^{-1}cm^2mol^{-1}$) is 60 in acetone. Selected FTIR absorptions (KBr, cm^{-1}): υ(SO), 1116(s), 1106(sh); υRu–Cl, 328(s); υRu–S, 402(m); υ(CH=N), 1616(s); υ(Ru–N) 272(s); υ(CH_2–CH_2) 908(m), 845(s). ^{1}H-NMR spectra: (δ in ppm): δ(Ar–H), 7.04–7.75(8H); δ(CH=N), 8.90(2H); δ(CH_3), 3.52(24H), 3.45(12H); δ(CH_2), 2.696(4H). $^{13}C\{^1H\}$-NMR: δ(CH_3), 45.08; 44.50; δ(CH=N) 162.68; δ(Ar-C) 126.52; δ(CH_2–CH_2) 112.42; 110.28.

2.4. *Synthesis of 3, [$(dmso)_2H$]$_2$[{***trans***-$RuCl_4(dmso)$}$_2$(2-ClBENEN)]*

[$(dmso)_2H$][(*trans*-$RuCl_4(dmso)_2$] was prepared as reported earlier [5]. Recrystallized [$(dmso)_2H$][(*trans*-$RuCl_4(dmso)_2$] (0.100 g, 0.18 mmol) was dissolved in 20 mL of ethanol and stirred with 2-ClBENEN (0.061 g, 0.20 mmol) for 6 h under inert atmosphere. Thereafter, 0.20 mmol of [$(dmso)_2H$][(*trans*-$RuCl_4(dmso)$]$_2$ was dissolved in 10 mL of ethanol and added to above reaction mixture and refluxed for 14 h. The reaction mixture was evaporated and reduced to half of its volume. A light brown black precipitate obtained was filtered and recrystallized from ethanol : acetone : ether (3 : 2 : 1) v/v, and dried in vacuum. Yield 0.189 g (75%) m.p. > 225°C. Found: C, 25.94; H, 3.86; N, 2.12; S, 15.16; $C_{28}H_{52}N_2S_6Cl_{10}O_6Ru_2$ ($M_\tau = 1259$) requires: C, 26.04; H, 3.92; N, 2.22; S, 15.22. Electronic spectra (λ_{max}, nm (ε in $M^{-1}cm^{-1}$)) in acetonitrile, 470(680), 390(960), 286(208), 210(968). $\mu_{eff} = 1.864\,\mu B$. ΔM at 25°C ($\Omega^{-1}cm^2mol^{-1}$) is 88 in acetone and 96 in water. Selected FTIR absorption

(KBr, cm^{-1}): υ(SO), 1108(s); υ(Ru–Cl), 332(s), 330(m); υ(Ru–S), 405(m); υ(CH=N), 1620(s), υ(Ru–N), 290(s), $\upsilon(CH_2–CH_2)$, 916(s), 848(sh); υ(H $\cdots$ O $\cdots$ H) 702(m).

2.5. *Synthesis of Complex* 4, *Na_2[*{**trans**-*$RuCl_4$(dmso)*}*$_2$(2-ClBENEN)]*

The starting complex Na[(*trans*-$RuCl_4(dmso)_2$] was prepared by literature procedure [5]. Recrystallized Na[(*trans*-$RuCl_4(dmso)_2$] (0.100 g, 0.24 mmol) and 2-ClBENEN (0.070 g, 0.23 mmol) were dissolved in 20 mL of methanol and stirred for 5 h under N_2(g). The initial red colour solution changes to light brown and 0.24 mmol of Na[(*trans*-$RuCl_4(dmso)_2$] was added and the reaction mixture was refluxed for 15 h. A black brown precipitate was obtained on evaporation which was recrystallized from 3 : 2 : 1 methanol : acetone : ether (v/v/v). Yield 0.186 g (78%) m.p. >225°C. Found: C, 23.96; H, 2.39; N, 2.80; S, 6.37; $C_{20}H_{24}N_2S_2O_2Cl_{10}Ru_2Na_2$ ($M_\tau = 989$) requires: C, 24.06; H, 2.42; N, 2.83; S, 6.47. Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile, 488(768), 400(929), 210(828); ΔM at 25°C ($\Omega^{-1}\,cm^{-1}\,mol^{-1}$) is 94 in acetone and 106 in water. $\mu_{eff} = 1.90\,\mu B$. Selected FTIR absorption (KBr, cm^{-1}); υ(SO), 1100(s); υ(Ru–Cl), 334(s), 330(sh); υ(Ru–S) 400(m); υ(CH=N), 1618.8(s), 1616(sh), υ(Ru–N) 288(s); $\upsilon(CH_2–CH_2)$ 918(s); 852(m).

2.6. *Synthesis of 5, [*{**cis**-*$RuCl_2(tmso)_3$*}*$_2$2-ClBENEN]*

cis-$RuCl_2(tmso)_4$ was prepared by literature procedure [4]. Recrystallized *cis*-$RuCl_2(tmso)_4$, (0.100 g, 0.17 mmol) and 2-ClBENEN (0.055 g, 0.18 mmol) were dissolved in 20 mL of ethanol and stirred for 6 h. The initial yellow solution changes to green; thereafter, 0.17 mmol of *cis*-$RuCl_2(tmso)_4$ was added and the reaction mixture was refluxed for 12 h. The greenish colour changes to reddish brown. On vacuum evaporation a black precipitate was obtained, which was recrystallized from 2 : 3 : 1 mixture of ethanol : acetone : ether (v/v/v) and vacuum dried. Yield 0.145 g (63%) m.p. >225°C. Found: C, 37.60; H, 4.76; N, 2.08; S, 14.98; $C_{40}H_{62}N_2O_6S_6Cl_6Ru_2$ ($M_\tau = 1273$) requires: C, 37.70; H, 4.87; N, 2.19; S, 15.31. Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 366(483), 319(350), 268(1108) 220(760). ΔM at 25°C ($\Omega^{-1}\,cm^{-1}\,mol^{-1}$) is 68 in acetone. Selected FTIR absorptions (KBr, cm^{-1}); υ(SO), 1120(s); 1108(sh); υ(Ru–Cl), 336(s), 332(sh); υ(Ru–S), 408(m); υ(CH=N), 1612(s); υ(Ru–N), 296(s); $\upsilon(CH_2–CH_2)$, 912(s), 858(m). ^{1}H-NMR (δ value in ppm): δ(Ar–H), 7.016–7.832(8H); δ(HC=N), 8.902(2H); $\delta(S–CH_2)$, 4.032(16H); 4.238(8H); $\delta(S–C–CH_2)$, 3.631(8H); 3.844(16H); $\delta(CH_2)$, 2.542(4H). $^{13}C\{^1H\}$NMR:δ(Ar–C), 125.628; δCH=N, 160.28; δ(S–C), 57.461, 56.322; δ(S–C–C) 26.206, 28.282; $\delta(CH_2–CH_2)$, 110.520, 111.640.

2.7. *Synthesis of 6, [*{*trans-$RuCl_2(tmso)_3$*}*$_2$2-ClBENEN]*

Recrystallized *trans*-$RuCl_2(tmso)_4$ [4] (0.100 g, 0.17 mmol) and 2-ClBENEN (0.055 g, 0.18 mmol) were dissolved in 20 mL of ethanol and stirred for 4 h. The initial yellow solution changes to light brown and then 0.17 mmol of *trans*-$RuCl_2(tmso)_4$ was added and refluxed for 8 h under inert atmosphere. On vacuum evaporation dark brown precipitate was obtained, which was recrystallized from 3 : 1, ethanol : acetone (v/v) and vacuum dried. Yield, 0.180 g (83%), m.p. > 225°C. Found: C, 37.62; H, 4.82; N, 2.09; S, 15.20; $C_{40}H_{62}N_2O_6S_6Cl_6Ru_2$ ($M_\tau = 1273$) requires C, 37.70; H, 4.87; N, 2.19; S, 15.31. Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetone, 452(400), 356(658), 308(820) 210(908). ΔM at 25°C ($\Omega^{-1}\,cm^{-1}\,mol^{-1}$) is 52 in acetone. Selected FTIR absorptions (KBr, cm^{-1}): υ(SO) 1138(s); 1110(sh); υ(Ru–Cl) 338(s), 330(sh); υ(Ru–S), 410(w); υ(CH=N), 1616.2(s); υ(Ru–N), 298(s); υ(CH_2–CH_2) 908(s), 845(m). ^{1}H-NMR (δ value in ppm): δ(Ar–H), 7.086–7.791(8H); δ(CH=N), 8.864(H), 8.965(H); δ(S–CH_2), 4.054(16H); δ 3.980(8H); δ(S–C–CH_2), 3.584(16H), 3.462(8H); δ(CH_2), 2.606(4H). $^{13}C\{^1H\}$NMR: δ(Ar–C), 124.021; δ(CH=N), 162.206; δ(CH_2–CH_2), 111.481, 110.601; δ(S–C), 57.620, 55.291; δ(S–C–C) 25.346, 26.282.

2.8. *Synthesis of 7, $[\{tmso)H]_2^+[(RuCl_4(tmso)\}_2(2\text{-ClBENEN})]$*

The [(tmso)H][*trans*-$RuCl_4(tmso)_2$] was prepared following literature procedure [4]. Recrystallized [(tmso)H][*trans*-$RuCl_4(tmso)_2$] (0.100 g, 0.17 mmol) and 2-ClBENEN (0.053 g, 0.17 mmol) were dissolved in 20 mL of ethanol and stirred for 6 h. The light red solution changes to green. Then, 0.17 mmol of [(tmso)H] [*trans*-$RuCl_4(tmso)_2$] was added and the reaction mixture refluxed for 12 h. On evaporation under vacuum a dark brown precipitate was obtained, which was recrystallized from acetone : ethanol : ether, 1 : 3 : 1 (v/v/v). Yield, 0.125 g (59%). m.p. > 225°C. Found: C, 30.86; H, 3.82; N, 2.19; S, 12.80; $C_{32}H_{48}N_2O_4S_4Cl_{10}Ru_2$ ($M_\tau = 1241$) requires: C, 30.94; H, 3.86; N, 2.20; S, 12.89. Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetone, 486(560), 406(900), 290(428), 280(308), 210(626). $\mu_{eff} = 1.94\,\mu B$. ΔM at 25°C ($\Omega^{-1}\,cm^{-1}\,mol^{-1}$) is 96 in acetone and 112 in water. Selected FTIR absorptions (KBr, cm^{-1}): υ(SO), 1135(s); υ(Ru–Cl), 336(s), 330(sh); υ(Ru–S) 414(w); υ(CH=N), 1619.3(s); υ(Ru–N), 301(s); υ(CH_2–CH_2), 912(s), 858(m); υ(O $\cdots$ H $\cdots$ O), 728(br).

3. Results and Discussion

Stoichiometry of **1–7** are in agreement with elemental analyses data. Molecular conductance of the complexes **1**, **2**, **5** and **6** were initially low for a very dilute (10^{-3} M) solution in water, but increases slowly on keeping the solution for 6–12 h, probably due to decomposition in solution [5]. However, molar conductance of the complexes **3**, **4** and **7** were high initially, indicating their ionic nature

Complex 1, 2, 5 and 6

These complexes are diamagnetic as expected for low spin ruthenium (II) complexes (low spin, d^6, $s = 0$). Complex **1** and **5** exhibit four bands in electronic spectra near 366 , 319 , 258 and 210 nm. The bands at about 366 and 319 nm were assigned to d–d transitions $^1A_{1g} \rightarrow {}^1T_{2g}$ and $^1A_{1g} \rightarrow {}^1T_{1g}$ respectively. The band near 258 nm can be assigned to intraligand transitions [19–22]. The sulphoxides exhibited a band near 210 nm [23]. Complex **2** and **6** also shows four bands in electronic spectra. The first two bands near 450 and 340 nm can be assigned to d–d transitions $^1A_{1g} \rightarrow {}^1T_{1g}$ and

$^1A_{1g} \rightarrow {}^1T_{2g}$, respectively, but could be MLCT transitions. The band near 300 nm can be assigned to an intraligand transition [19–22].

FTIR spectra of dmso analogues show one or two peaks for υ(SO) near $1100\,cm^{-1}$ and the tmso analogues at $1120\,cm^{-1}$; in each case a positive shift in comparison to free dmso/tmso was observed, indicative of coordination of dmso to the ruthenium [22, 23]. A new band for υM-S at $401\,cm^{-1}$, confirms this. A sharp IR active band at $1640\,cm^{-1}$ in the ligand, characteristic of the azomethine group of the Schiff base, shifted to lower wavenumber (about $1620\,cm^{-1}$) with less intensity. The shift of υ(CH=N) to lower frequency indicates coordination of azomethine nitrogen to metal, confirmed by υ(Ru–N) at $270\,cm^{-1}$ [24, 25]. However, the shift of υ(CH=N) was less ($\sim 20\,cm^{-1}$) than expected ($\sim 40\,cm^{-1}$), perhaps due to the bridging mode. The sharp peak near $332\,cm^{-1}$ is assigned for υ(RuCl). The two sharp and medium bands near $912\,cm^{-1}$ and $842\,cm^{-1}$ for rocking mode of $\upsilon(CH_2–CH_2)$ indicated that the two $–CH_2$ groups were gauche [26].

^{1}H-NMR spectra of all the above complexes display a multiplet between δ 7.016–7.832 ppm for 8H of the two substituted aromatic benzene rings. Similarly, each complex has one δ(CH=N) at δ 8.864 ppm for two protons, indicating symmetrical environment around each azomethine group. In **1** two singlets at δ 3.50 and δ 3.41 ppm were observed for $\delta(CH_3)$. The signal at δ 3.41 ppm for 24H was assigned for methyl of dmso *trans* to each other and the signal at δ 3.50 ppm for 12H was assigned for methyl group of dmso *trans* to Cl atom. Similarly, in complex **2** two signals were observed for $\delta(CH_3)$. The signal at δ 3.52 ppm for 24H was assigned for the methyl of dmso *trans* to each other and the signal at δ 3.45 ppm for 12H was assigned for the methyl of dmso *trans* to azomethine (CH=N). In complex **5** two signals were observed for $\delta(S–CH_2)$ at δ 4.032 and δ 4.238 ppm. The signal at δ 4.032 ppm for 16H was assigned for the tmso *trans* to each other and the signal at δ 4.238 ppm for 8H was assigned for tmso *trans* to Cl. Similarly, two signals at δ 3.631 and δ 3.844 ppm for 16 and 8H, were assigned for the $\delta(S–C–CH_2)$ of the tmso's *trans* to each other and the tmso *trans* to Cl, respectively. In **6** two signals for $\delta(S–CH_2)$, at δ 4.054 and δ 3.980 ppm were assigned for the tmso's *trans* to each other and for the tmso *trans* to azomethine, respectively.

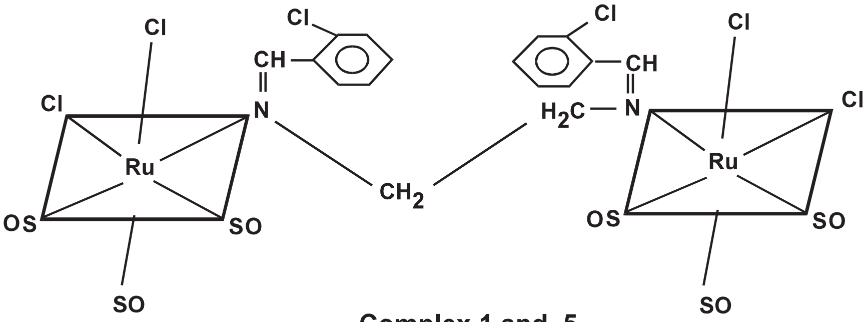
All the complexes exhibit a signal near δ 2.362 ppm for 4H, attributed to two CH_2-groups.

^{13}C{^{1}H}NMR of **1** has signals at δ 44.06 and δ 45.68 ppm assigned for methyl carbon of dmso *trans* to each other and methyl carbon of dmso *trans* to Cl for **2**, δ 45.08 and δ 44.50 ppm, assigned for dmso *trans* to each other and methyl carbon of dmso *trans* to azomethine group.

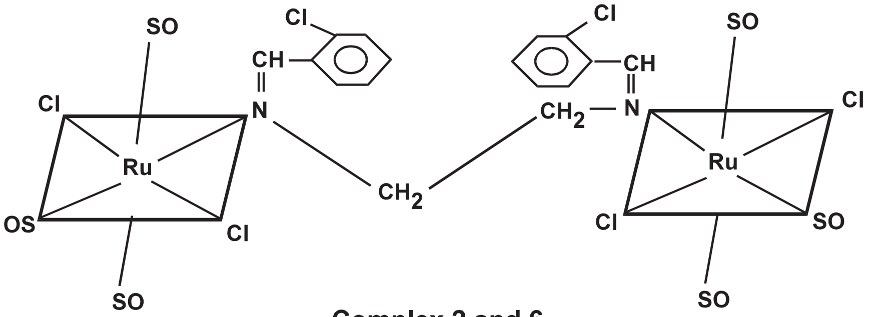
Similarly, **5**, the tmso analogue of **1** shows **2** signals for δ(S–C) at δ 57.461 and δ 56.322 ppm, assigned for the $–S–CH_2$ of carbon of tmso *trans* to Cl and *trans* to each other. This complex also has signals at δ 26.206 and δ 28.282 ppm assigned to $S–C–CH_2$ carbon of tmso *trans* to each other and *trans* to Cl. Complex **6** has similar assignments.

All complexes have one signal at δ 160.00 ppm assigned for two (CH=N) carbons in the same environment, as evident from ^{1}H-NMR spectra. The signal for aromatic carbon was centered in each case as a multiplet near δ 125.00 ppm.

Surprisingly, ^{13}C{^{1}H}NMR shows two signals for $\delta(CH_2–CH_2)$ carbon at about δ 111 ppm and δ 110 ppm indicating that the two $–CH_2$ groups are in



Complex 1 and 5



Complex 2 and 6

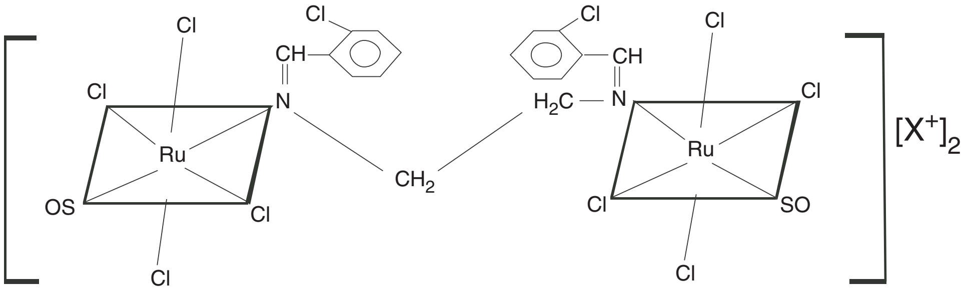
Figure 1. SO = dmso in complex **1** and **2** and tmso in complex **5** and **6**.

different environments. Thus, on the basis of electronic, FTIR, ^{1}H-NMR and ^{13}C{^{1}H}NMR spectra we suggest the most plausible structure as shown in figure 1.

Complexes 3, 4 and 7

These complexes were paramagnetic with a magnetic moment 1.86–1.94 μB, lower than the normal value (2.10 μB). The low μ_{eff} values may be due to factors including the presence of low symmetry ligand fields, metal–metal interactions and the formation of molecular orbital by extended overlap of metal and ligand orbital [27, 28]. The magnetic moment of complexes of T_{2g} ground term are lowered due to progressive quenching of the orbital angular momentum by spin orbital coupling, removing the degeneracy of the triplet ground term. Extensive spin orbit coupling can reduce the moment below the spin only value [29].

Electronic spectra of **3** have five bands. An intense absorption at about 390 nm coupled with a less intense band at $\lambda_{\max}$ 470 nm, are ascribed to charge transfer transitions from chlorides to Ru(III), typical for the $RuCl_4^-$. Weak absorptions at 286 and 290 nm, are probably due to protonated sulphoxide [31]. However **4** shows only three bands in electronic spectra. The first two bands, at 400 and 488 nm were assigned as for **3** and the band at 210 nm, present in all the complexes, is characteristic of sulphoxide [21]. On the basis of FTIR, UV-Vis and elemental analyses, we suggested structures as shown in figure 2.



Complex **3**, **4** and **7**

Figure 2. SO = dmso for complex **3** and **4** and tmso for complex **7**, $[x^+] = [(\text{dmso})_2\text{H}]^+$ for complex **3**, Na^+ for complex **4** and $[(\text{tmso})\text{H}]^+$ for complex **7**.

4. Conclusions

Chemoselective and tailored use of a schiff base in reaction with ruthenium sulphoxide can act as a spacer bridge between two ruthenium sulphoxide units. These complexes are novel and find importance due to their biological relevance.

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