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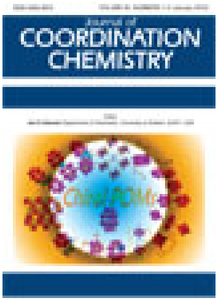

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Spectroscopic characterization of Schiff base coordinating monomolecular trinuclear complexes prepared through tailored synthesis

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Spectroscopic characterization of Schiff base coordinating monomolecular trinuclear complexes prepared through tailored synthesis

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A new *bis-N*,*N*′-bidentate Schiff base has been synthesized, characterized, and used in the synthesis of Ru^{II} and Rh^{II} complexes, which were further applied as precursors in the preparation of trinuclear complexes. These complexes were characterized by elemental analyses, molar conductance measurements, magnetic susceptibility, FTIR, TGA, FAB-mass, ESI-MS, ^{1}H-NMR, ^{13}C{^{1}H}-NMR, ^{1}H-^{1}H COSY 2D-NMR, and electronic spectral studies. In complexes, one metal center is coordinated through azomethine nitrogen of *bis-N*,*N*′-bidentate Schiff base and the other two metal ions are coordinated through nitrogen of pyridine.

Keywords: Monomolecular complexes; Rhodium; Ruthenium; Schiff base; Tailored synthesis

1. Introduction

The rational design and synthesis of new solids with organized molecular frameworks and desirable structural and functional features is a major goal [1]. Metal-containing supramolecules and coordination polymers have attracted interest because there are many promising metal fragments available for construction of supramolecular materials [2]. The homo and hetero coordinated multi-centered metal complexes are known for magnetic, electronic, electrochemical, photo-optical, and catalytic properties [3].

Several ruthenium compounds with coordinated dimethylsulfoxide have been shown to possess good antitumor and antimetastatic properties against animal models. Among these a Ru(III) complex, NAMI-A, is well-known for its good antimetastatic activity [4–12]. $[Rh(phen)_2(phi)]^{3+}$ and $[Ru(bpy)_2(dppz)]^{3+}$ were accepted as probes and are proposed to be metallo-intercalators for mismatch recognition in DNA base pairs during DNA replication [13, 14].

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We were interested to prepare Ru/Rh-containing trinuclear monomolecular complexes based on quasi-octahedral geometries bearing Schiff-base ligands; Schiff bases represent one of the most widely utilized classes of ligand in metal coordination chemistry, finding importance in catalytic applications [15], and various biological systems [16–18]. Development of a simple synthetic method to assemble commercially available starting material is also important to extend the range of coordinating structures in solution. From this synthetic strategy we have focused on a *bis*-N,N'-bidentate Schiff base of isoniazid and synthesized 12 ruthenium- and rhodium-containing complexes.

2. Experimental

$RuCl_3 \cdot 3H_2O$ (E. Merck), $RhCl_3 \cdot 3H_2O$ (E. Merck), tetramethylenesulfoxide (Lancaster, UK), and *o*-phenylenediamine (E. Merck) were used as received. Analytical grade dimethyl sulfoxide (E. Merck) and routine solvents were used without purification for synthetic purposes.

Electronic absorption spectra were recorded with a Shimadzu-1700 UV-Vis spectrophotometer equipped with a PC. Conductivity measurements were carried out at 25°C on an EI-181 conductivity bridge with a dipping type cell. FTIR spectra were recorded in KBr pellets on a Shimadzu-8400 PC FTIR spectrophotometer. ^{1}H-NMR, $^{13}C\{^1H\}$-NMR, and 2D-NMR (^{1}H-^{1}H COSY) spectra were recorded in acetone on a Bruker DRX-300 NMR spectrometer. Gouy's method was employed for measurement of magnetic susceptibility; $Hg[Co(NCS)_4]$ was used as standard. Diamagnetic correction was made using Pascal's constants. Elemental analyses (C, H, N) were performed on an Elementar Vario EL III Elemental analyzer. FAB-mass spectra were recorded on a Jeol SX-102 mass spectrometer using NBA as matrix. Thermogravimetric data were in air at $10^\circ C\,min^{-1}$ from 25°C to 750°C using a Shimadzu TGA-50H analyzer. An ESI-MS spectrum was recorded on an Agilent 6520 Q-Tof mass spectrometer in acetonitrile.

2.1. *Synthesis of Schiff base ligand*

Ligand was synthesized by Schiff base condensation between isoniazid (INH) and benzaldehyde with 1 : 1 ratio using standard procedure [19]. Schiff base of INH (1.3908 g, 6.2 mmol) was dissolved in 25 mL absolute EtOH; to this solution *o*-phenylenediamine (0.3352 g, 3.1 mmol) in EtOH (10 mL) was added and the reaction mixture was kept under reflux for 5 h in an inert atmosphere. Color of the reaction mixture changed from golden yellow to blood red. Dirty yellow solid was precipitated, on transfer of blood red transparent solution (drop by drop) into ice cold water, which was filtered off, washed with cold EtOH, and dried under vacuum. It was recrystallized from ethanol/water/acetone, 3 : 1 : 2, v/v, to obtain dirty yellow shining crystals. Yield: 4.6548 g (64.7%). Found: C, 73.28; H, 5.06; N, 21.68; $C_{32}H_{26}N_8$ ($M_\tau = 522$). Requires: C, 73.54; H, 5.01; N, 21.44. Selected infrared absorption (KBr, cm^{-1}): ν(N–H), 3436(w); ν(CH=N), 1635(s); ν(C=N), 1598(s). ^{1}H-NMR (300 MHz, δ, acetone): 11.18(s, 2H, =N–NH); 8.84(s, 2H, CH=N); 8.62–6.97(m, 22H, Ar–H). $^{13}C\{^1H\}$-NMR

(300 MHz, δ, acetone): 168.6(CH=N), 169.3(C=N); 133.6–122.8(Ar–C). FAB-MS $[C_{32}H_{26}N_8 + H]^+$ $m/z = 523$.

2.2. *Synthesis of complexes*

2.2.1. Preparation of Schiff base ruthenium precursors (1). A hot ethanolic (20 mL) solution of the Schiff base (0.5226 g, 0.1 mmol) and a hot ethanolic (20 mL) solution of $RuCl_3 \cdot 3H_2O$ (0.0261 g, 0.1 mmol) were mixed together with constant stirring. The reaction mixture was refluxed for 12 h at ~75°C. On cooling, dark brown product formed which was filtered off, washed with cold ethanol, and dried under vacuum over fused calcium chloride. Purity of product was checked by TLC. Yield: 0.2054 g (77.3%); m.p. > 220°C; Found: C, 55.52; H, 3.71; N, 16.20; $C_{32}H_{26}N_8Cl_2Ru$ ($M_\tau = 694$). Requires: C, 55.34; H, 3.77; N, 16.13. Selected infrared absorption (KBr, cm^{-1}): ν(N–H), 3438(w); ν(CH=N), 1621(s); ν(C=N), 1578(s); ν(M–Cl), 335(s); ν(M–N), 278(s). Electronic spectra (λ_{max}, nm (ε in $(mol\,L^{-1})\,cm^{-1}$)) in acetonitrile: 678(72), 530(216), 414(569), 340(948), 296(1098). Δm at 25°C (Ω^{-1} in $(mol\,L^{-1})\,cm^{-1}$): 52 in DMSO, 98 in acetonitrile, 138 in acetone. ^{1}H-NMR (300 MHz, δ, acetone): 11.13(s, 2H, =N–NH); 9.02(s, 2H, CH=N); 8.96-6.88(m, 22H, Ar–H). $^{13}C\{^1H\}$-NMR (300 MHz, δ, acetone): 170.2(CH=N), 170.8(C=N); 134.0–121.2(Ar–C). FAB-MS (m/z): $[C_{32}H_{26}N_8Cl_2Ru^{104}]^+ = 697$, $[C_{32}H_{26}N_8Cl_2Ru + H]^+ = 695$, $[C_{32}H_{26}N_8Cl_2Ru^{96}]^+ = 689$, $[C_{32}H_{26}N_8Cl_2Ru–Cl]^+ = 659$, $[C_{32}H_{26}N_8 + H]^+ = 523$, $[RuCl_2]^+ = 172$.

2.2.1.1. *Preparation of* **2**. Complex **1** (0.0695 g, 0.1 mmol) dissolved in acetone 15 mL was added to precursor complex [*cis*, *fac*-$RuCl_2(S\text{-}dmso)_3(O\text{-}dmso)$] [20], (0.2 mmol) in 20 mL acetone and refluxed for 4–6 h. After cooling the precipitate was filtered off and washed with water. Color: Black, Yield: 0.1245 g (79.9%); m.p. > 220°C; Found: C, 35.11; H, 4.18; N, 7.52; S, 12.82; $C_{44}H_{62}N_8S_6O_6Cl_6Ru_3$ ($M_\tau = 1507$). Requires: C, 35.06; H, 4.15; N, 7.43; S, 12.76. Selected infrared absorption (KBr, cm^{-1}): ν(N–H), 3442(w); ν(CH=N), 1613(s); ν(C=N), 1581(s); ν(SO), 1101(s); ν(M–S), 407(m); ν(M–Cl), 333(s); ν(M–N), 283(s). Electronic spectra (λ_{max}, nm (ε in $(mol\,L^{-1})\,cm^{-1}$)) in acetonitrile: 663(58), 532(298), 402(582), 302(963). Δm at 25°C (Ω^{-1} in $(mol\,L^{-1})\,cm^{-1}$): 46 in DMSO, 101 in acetonitrile, 142 in acetone. ^{1}H-NMR (300 MHz, δ, acetone): 11.17(s, 2H, =N–NH); 9.13(s, 2H, CH=N); 8.84–6.93(m, 22H, Ar–H); 3.52(s, 12H, CH_3); 3.49(s, 12H, CH_3); 3.42(s, 12H, CH_3). $^{13}C\{^1H\}$-NMR (300 MHz, δ, acetone): 170.0(CH=N), 170.4(C=N); 133.1–120.3(Ar–C); 45.8 (S–C); 44.9(S–C); 43.6(S–C). FAB-MS (m/z): $[C_{44}H_{62}N_8S_6O_6Cl_6^{37}Ru_3]^+ = 1519$, $[C_{44}H_{62}N_8S_6O_6Cl_6Ru_3^{104}]^+ = 1516$, $[C_{44}H_{62}N_8S_6O_6Cl_6Ru_3 + H]^+ = 1508$, $[C_{44}H_{62}N_8S_6O_6Cl_6Ru_3^{96}]^+ = 1492$, $[C_{32}\,H_{26}N_8 + H]^+ = 523$.

2.2.1.2. *Preparation of* **3**. Complex **3** was obtained from [*trans*-$RuCl_2(S\text{-}dmso)_4$] [21], (0.2 mmol) in a manner similar to that used for synthesis of **2**. Color: Black, Yield: 0.1068 g (68.6%); m.p. > 220°C; Found: C, 35.09; H, 4.12; N, 7.45; S, 12.78; $C_{44}H_{62}N_8S_6O_6Cl_6Ru_3$ ($M_\tau = 1507$). Requires: C, 35.06; H, 4.15; N, 7.43; S, 12.76. Selected infrared absorption (KBr, cm^{-1}): ν(N–H), 3430(w); ν(CH=N), 1622(s); ν(C=N), 1588(s); ν(SO), 1099(s); ν(M–S), 406(m); ν(M–Cl), 334(s); ν(M–N), 278(s). Electronic spectra (λ_{max}, nm (ε in $(mol\,L^{-1})\,cm^{-1}$)) in acetonitrile: 669(64), 528(244), 418(602), 328(992), 294(1046). Δm at 25°C (Ω^{-1} in $(mol\,L^{-1})\,cm^{-1}$): 68 in DMSO, 104 in acetonitrile, 152 in acetone. ^{1}H-NMR (300 MHz, δ, acetone): 11.14(s, 2H, =N–NH); 9.18(s, 2H, CH=N); 8.98–7.06(m, 22H, Ar–H); 3.43(s, 12H, CH_3); 3.32(s, 24H, CH_3). $^{13}C\{^1H\}$-NMR (300 MHz, δ, acetone): 169.8(CH=N), 170.1(C=N); 134.8–120.9(Ar–C); 45.3(S–C); 44.6(S–C). FAB-MS (*m*/*z*): $[C_{44}H_{62}N_8S_6O_6Cl_6^{37}Ru_3]^+ = 1519$, $[C_{44}H_{62}N_8S_6O_6Cl_6Ru_3^{104}]^+ = 1516$, $[C_{44}H_{62}N_8S_6O_6Cl_6Ru_3 + H]^+ = 1508$, $[C_{44}H_{62}N_8S_6O_6Cl_6Ru_3^{96}]^+ = 1492$, $[C_{32}H_{26}N_8 + H]^+ = 523$.

2.2.1.3. *Preparation of* **4**. Complex **4** was obtained from [*cis*-$RuCl_2$(S-tmso)$_4$] [22], (0.2 mmol) in a manner similar to that used for the synthesis of **2**. Color: Black, Yield: 0.0989 g (70.0%); m.p. > 220°C; Found: C, 40.51; H, 4.40; N, 6.70; S, 11.66; $C_{56}H_{74}N_8S_6O_6Cl_6Ru_3$ ($M_\tau = 1663$). Requires: C, 40.43; H, 4.48; N, 6.74; S, 11.56. Selected infrared absorption (KBr, cm^{-1}): ν(N–H), 3445(w); ν(CH=N), 1624(s); ν(C=N), 1582(s); ν(SO), 1122(s); ν(M–S), 398(m); ν(M–Cl), 336(s); ν(M–N), 275(s). Electronic spectra (λ_{max}, nm (ε in (mol L^{-1}) cm^{-1})) in acetonitrile: 687(82), 546(276), 413(548), 304(1006). Δm at 25°C (Ω^{-1} in (mol L^{-1}) cm^{-1}): 56 in DMSO, 102 in acetonitrile, 134 in acetone. ^{1}H-NMR (300 MHz, δ, acetone): 11.20(s, 2H, =N–NH); 9.14(s, 2H, CH=N); 8.80–6.98(m, 22H, Ar–H); 4.06(m, 8H, S–CH_2); 4.01(m, 8H, S–CH_2); 3.51(m, 8H, S–CH_2); 2.31(m, 24H, S–C–CH_2). $^{13}C\{^1H\}$-NMR (300 MHz, δ, acetone): 169.3(CH=N), 169.9(C=N); 133.4–121.0(Ar–C); 57.8 (S–C); 57.4(S–C); 55.9(S–C); 27.3(S–C–C); 26.8(S–C–C); 25.1(S–C–C). FAB-MS (*m*/*z*): $[C_{56}H_{74}N_8S_6O_6Cl_6^{37}Ru_3]^+ = 1675$, $[C_{56}H_{74}N_8S_6O_6Cl_6Ru_3^{104}]^+ = 1672$, $[C_{56}H_{74}N_8S_6O_6Cl_6Ru_3^{96}]^+ = 1648$, $[C_{56}H_{74}N_8S_6O_6Cl_6Ru_3 + H]^+ = 1664$, $[C_{32}H_{26}N_8 + H]^+ = 523$.

2.2.1.4. *Preparation of* **5**. Complex **5** was obtained from [*trans*-$RuCl_2$(S-tmso)$_4$] [22], (0.2 mmol) in a manner similar to that used for **2**. Color: Black, Yield: 0.0964 g (68.2%); m.p. > 220°C; Found: C, 40.38; H, 4.51; N, 6.78; S, 11.60; $C_{56}H_{74}N_8S_6O_6Cl_6Ru_3$ ($M_\tau = 1663$). Requires: C, 40.43; H, 4.48; N, 6.74; S, 11.56. Selected infrared absorption (KBr, cm^{-1}): ν(N–H), 3435(w); ν(CH=N), 1617(s); ν(C=N), 1586(s); ν(SO), 1128(s); ν(M–S), 401(m); ν(M–Cl), 332(s); ν(M–N), 274(s). Electronic spectra (λ_{max}, nm (ε in (mol L^{-1}) cm^{-1})) in acetonitrile: 686(86), 534(268), 420(596), 336(1044), 299(1123). Δm at 25°C (Ω^{-1} in (mol L^{-1}) cm^{-1}): 73 in DMSO, 109 in acetonitrile, 154 in acetone. ^{1}H-NMR (300 MHz, δ, acetone): 11.15(s, 2H, =N–NH); 9.10(s, 2H, CH=N); 8.94–6.83(m, 22H, Ar–H); 3.98(m, 8H, S–CH_2); 3.53(m, 16H, S–CH_2); 3.36(m, 24H, S–C–CH_2). $^{13}C\{^1H\}$-NMR (300 MHz, δ, acetone): 170.1(CH=N), 170.7(C=N); 134.7–119.8(Ar–C); 57.2(S–C); 55.8(S–C); 27.0(S–C–C); 25.4(S–C–C). FAB-MS (*m*/*z*): $[C_{56}H_{74}N_8S_6O_6Cl_6^{37}Ru_3]^+ = 1675$, $[C_{56}H_{74}N_8S_6O_6Cl_6Ru_3^{104}]^+ = 1672$, $[C_{56}H_{74}N_8S_6O_6Cl_6Ru_3 + H]^+ = 1664$, $[C_{56}H_{74}N_8S_6O_6Cl_6Ru_3^{96}]^+ = 1648$, $[C_{32}H_{26}N_8 + H]^+ = 523$.

2.2.1.5. *Preparation of* **6**. Complex **6** was obtained from [*mer*-$RhCl_3$(S-dmso)$_2$(O-dmso)] [23], (0.2 mmol) in a manner similar to that used for synthesis of **2**. Color: Blackish-brown, Yield: 0.0898 g (55.9%); m.p. > 220°C; Found: C, 33.78; H, 3.56; N, 7.80; S, 9.08; $C_{40}H_{50}N_8S_4O_4Cl_8RuRh_2$ ($M_\tau = 1425$). Requires: C, 33.70; H, 3.54; N, 7.86; S, 8.99. Selected infrared absorption (KBr, cm^{-1}): ν(N–H), 3428(w); ν(CH=N), 1614(s); ν(C=N), 1583(s); ν(SO), 1096(s); ν(M–S), 402(m); ν(M–Cl), 352(s), 330(s); ν(M–N), 282(s). Electronic spectra (λ_{max}, nm (ε in (mol L^{-1}) cm^{-1})) in acetonitrile: 675(66), 541(258), 407(609), 298(1128). Δm at 25°C (Ω^{-1} in (mol L^{-1}) cm^{-1}): 58 in DMSO, 111 in acetonitrile, 124 in acetone. ^{1}H-NMR (300 MHz, δ, acetone): 11.22(s, 2H, =N–NH); 9.08(s, 2H, CH=N); 8.83–6.85(m, 22H, Ar–H); 3.48(s, 12H, CH_3);

3.36(s, 12H, CH_3). $^{13}C\{^1H\}$-NMR (300 MHz, δ, acetone): 169.8(CH=N), 170.3(C=N); 132.9–117.3(Ar–C); 45.7 (S–C); 44.8(S–C). FAB-MS (*m*/*z*): $[C_{40}H_{50}N_8S_4O_4Cl_8^{37}RuRh_2]^+ = 1441$, $[C_{40}H_{50}N_8S_4O_4Cl_8RuRh_2^{103}]^+ = 1429$, $[C_{40}H_{50}N_8S_4O_4Cl_8RuRh_2 + H]^+ = 1426$, $[C_{40}H_{50}N_8S_4O_4Cl_8Ru^{96}Rh_2]^+ = 1420$, $[C_{32}H_{26}N_8 + H]^+ = 523$.

2.2.1.6. *Preparation of 7*. Complex **7** was obtained from [*mer*-$RhCl_3$(S-tmso)$_2$(O-tmso)] [23], (0.2 mmol) in a manner similar to that used for **2**. Color: Blackish-brown, Yield: 0.1144 g (78.0%); m.p. > 220°C; Found: C, 37.74; H, 3.84; N, 7.40; S, 8.44; $C_{48}H_{58}N_8S_4O_4Cl_8RuRh_2$ ($M_\tau = 1529$). Requires: C, 37.69; H, 3.82; N, 7.32; S, 8.38. Selected infrared absorption (KBr, cm^{-1}): ν(N–H), 3440(w); ν(CH=N), 1619(s); ν(C=N), 1581(s); ν(SO), 1118(s); ν(M–S), 400(m); ν(M–Cl), 354(s), 338(s); ν(M–N), 275(s). Electronic spectra (λ_{max}, nm (ε in $(mol\,L^{-1})\,cm^{-1}$)) in acetonitrile: 682(78), 548(232), 404(561), 307(1093). Δm at 25°C (Ω^{-1} in $(mol\,L^{-1})\,cm^{-1}$): 64 in DMSO, 113 in acetonitrile, 140 in acetone. ^1H-NMR (300 MHz, δ, acetone): 11.16(s, 2H, =N–NH); 9.12(s, 2H, CH=N); 8.95–7.02(m, 22H, Ar–H); 3.96(m, 8H, S–CH_2); 3.68(m, 8H, S–CH_2); 2.48(m, 16H, S–C–CH_2). $^{13}C\{^1H\}$-NMR (300 MHz, δ, acetone): 170.1 (CH=N), 170.9(C=N); 134.6–121.1(Ar–C); 57.6 (S–C); 56.2(S–C); 26.9(S–C–C); 25.3(S–C–C). FAB-MS (*m*/*z*): $[C_{40}H_{58}N_8S_4O_4Cl_8^{37}RuRh_2]^+ = 1545$, $[C_{48}H_{58}N_8S_4O_4Cl_8RuRh_2^{103}]^+ = 1533$, $[C_{48}H_{58}N_8S_4O_4Cl_8RuRh_2 + H]^+ = 1530$, $[C_{48}H_{58}N_8S_4O_4Cl_8Ru^{96}Rh_2]^+ = 1524$, $[C_{32}H_{26}N_8 + H]^+ = 523$.

2.2.2. Preparation of Schiff base rhodium precursor (8). A hot ethanolic (20 mL) solution of the Schiff base (0.5226 g, 0.1 mmol) and a hot ethanolic (20 mL) solution of $RhCl_3 \cdot 3H_2O$ (0.0263 g, 0.1 mmol) were mixed together with constant stirring. The reaction mixture was refluxed for 8 h at ~75°C. On cooling, dark brown red product formed, was filtered off, washed with cold ethanol, and dried under vacuum over fused calcium chloride. Purity of product was checked by TLC. Yield: 0.2189 g (82.8%); m.p. > 220°C; Found: C, 55.22; H, 3.80; N, 16.14; $C_{32}H_{26}N_8Cl_2Rh$ ($M_\tau = 696$). Requires: C, 55.19; H, 3.76; N, 16.09. Selected infrared absorption (KBr, cm^{-1}): ν(N–H), 3446(w); ν(CH=N), 1623(s); ν(C=N), 1587(s); ν(M–Cl), 356(s); ν(M–N), 280(s). Electronic spectra (λ_{max}, nm (ε in $(mol\,L^{-1})\,cm^{-1}$)) in acetonitrile: 478(126), 406(302), 332(763), 302(984). $\mu_{eff} = 1.87\,\mu B$; Δm at 25°C (Ω^{-1} in $(mol\,L^{-1})\,cm^{-1}$): 12 in DMSO, 53 in acetonitrile, 12 in acetone. FAB-MS (*m*/*z*): $[C_{32}H_{26}N_8Cl_2^{37}Rh]^+ = 700$, $[C_{32}H_{26}N_8Cl_2Rh + H]^+ = 697$, $[C_{32}H_{26}N_8Cl_2Rh\text{-}Cl]^+ = 661$, $[C_{32}H_{26}N_8 + H]^+ = 523$, $[RhCl_2]^+ = 173$.

2.2.2.1. *Preparation of 9*. Complex **8** (0.0696 g, 0.1 mmol) dissolved in acetone 15 mL was added to $[(dmso)_2H]^+[\textit{trans}\text{-}RuCl_4(dmso)_2]^-$ [24], (0.2 mmol) in 20 mL acetone and refluxed for 4–5 h. After cooling the precipitate was filtered off and washed with water. Color: Blackish-brown, Yield: 0.1165 g (78.4%); m.p. > 220°C; Found: C, 31.90; H, 3.92; N, 6.81; S, 11.72; $C_{44}H_{64}N_8S_6O_6Cl_{10}Ru_2Rh$ ($M_\tau = 1653$). Requires: C, 31.97; H, 3.90; N, 6.78; S, 11.64. Selected infrared absorption (KBr, cm^{-1}): ν(N–H), 3441(w); ν(CH=N), 1625(s); ν(C=N), 1579(s); ν(SO), 1098(s), 1054(s); $\nu[(dmso)_2H]^+$, 728(br s); ν(M–S), 397(m); ν(M–Cl), 352(s), 335(s); ν(M–N), 288(s). Electronic spectra (λ_{max}, nm (ε in $(mol\,L^{-1})\,cm^{-1}$)) in acetonitrile: 483(148), 410(284), 335(782), 300(1002). $\mu_{eff} = 1.72\,\mu B$; Δm at 25°C (Ω^{-1} in $(mol\,L^{-1})\,cm^{-1}$): 126 in DMSO. FAB-MS (*m*/*z*): $[C_{44}H_{64}N_8S_6O_6Cl_{10}^{37}Ru_2Rh]^+ = 1673$,

$[\mathrm{C_{44}H_{64}N_8S_6O_6Cl_{10}Ru_2^{104}Rh}]^+ = 1659$, $[\mathrm{C_{44}H_{64}N_8S_6O_6Cl_{10}Ru_2Rh^{103}}]^+ = 1655$, $[\mathrm{C_{44}H_{64}N_8S_6O_6Cl_{10}Ru_2Rh + H}]^+ = 1654$, $[\mathrm{C_{44}H_{64}N_8S_6O_6Cl_{10}Ru_2^{96}Rh}]^+ = 1643$, $[\mathrm{C_{32}H_{26}N_8 + H}]^+ = 523$.

2.2.2.2. *Preparation of* ***10***. Complex **10** was obtained from $[\mathrm{Na}]^+[trans\text{-}\mathrm{RuCl_4(dmso)_2}]^-$ [24], (0.2 mmol) in a manner similar to that used for **9**. Color: Blackish-brown, Yield: 0.1345 g (82.1%); m.p. > 220°C; Found: C, 31.30; H, 2.75; N, 8.15; S, 4.71; $\mathrm{C_{36}H_{38}N_8S_2O_2Cl_{10}Na_2Ru_2Rh}$ ($M_\tau = 1384$). Requires: C, 31.23; H, 2.77; N, 8.09; S, 4.63. Selected infrared absorption (KBr, $\mathrm{cm^{-1}}$): ν(N–H), 3447(w); ν(CH=N), 1615(s); ν(C=N), 1577(s); ν(SO), 1108(s); ν(M–S), 399(m); ν(M–Cl), 356(s), 333(s); ν(M–N), 281(s). Electronic spectra ($\lambda_{\max}$, nm (ε in $(\mathrm{mol\,L^{-1}})\,\mathrm{cm^{-1}}$)) in acetonitrile: 472(139), 397(296), 340(744), 303(963). $\mu_{\mathrm{eff}} = 1.78\,\mu\mathrm{B}$; Δm at 25°C (Ω^{-1} in $(\mathrm{mol\,L^{-1}})\,\mathrm{cm^{-1}}$): 118 in DMSO. FAB-MS ($m/z$): $[\mathrm{C_{36}H_{38}N_8S_2O_2Cl_{10}Na_2Ru_2Rh + Na}]^+ = 1407$, $[\mathrm{C_{36}H_{38}N_8S_2O_2Cl_{10}^{37}Na_2Ru_2Rh}]^+ = 1404$, $[\mathrm{C_{36}H_{38}N_8S_2O_2Cl_{10}Na_2Ru_2^{104}Rh}]^+ = 1390$, $[\mathrm{C_{36}H_{38}N_8S_2O_2Cl_{10}Na_2Ru_2Rh^{103}}]^+ = 1385$, $[\mathrm{C_{36}H_{38}N_8S_2O_2Cl_{10}Na_2Ru_2^{96}Rh}]^+ = 1374$, $[\mathrm{C_{32}H_{26}N_8 + H}]^+ = 523$.

2.2.2.3. *Preparation of* ***11***. Complex **11** was obtained from $[\mathrm{(tmso)H}]^+[trans\text{-}\mathrm{RuCl_4(tmso)_2}]^-$ [22], (0.2 mmol) in a manner similar to that used in synthesis of **9**. Color: Blackish-brown, Yield: 0.0987 g (68.6%); m.p. > 220°C; Found: C, 31.10; H, 3.80; N, 6.89; S, 8.06; $\mathrm{C_{48}H_{60}N_8S_4O_4Cl_{10}Ru_2Rh}$ ($M_\tau = 1600$). Requires: C, 31.01; H, 3.78; N, 6.99; S, 8.01. Selected infrared absorption (KBr, $\mathrm{cm^{-1}}$): ν(N–H), 3433(w); ν(CH=N), 1620(s); ν(C=N), 1582(s); ν(SO), 1126(s), 1028(s); $\nu[\mathrm{(tmso)H}]^+$, 724(brs); ν(M–S), 403(m); ν(M–Cl), 351(s), 337(s); ν(M–N), 280(s). Electronic spectra ($\lambda_{\max}$, nm (ε in $(\mathrm{mol\,L^{-1}})\,\mathrm{cm^{-1}}$)) in acetonitrile: 486(142), 399(278), 344(792), 299(998). $\mu_{\mathrm{eff}} = 1.67\,\mu\mathrm{B}$; Δm at 25°C (Ω^{-1} in $(\mathrm{mol\,L^{-1}})\,\mathrm{cm^{-1}}$): 138 in DMSO. FAB-MS ($m/z$): $[\mathrm{C_{48}H_{60}N_8S_4O_4Cl_{10}^{37}Ru_2Rh}]^+ = 1620$, $[\mathrm{C_{48}H_{60}N_8S_4O_4Cl_{10}Ru_2^{104}Rh}]^+ = 1606$, $[\mathrm{C_{48}H_{60}N_8S_4O_4Cl_{10}Ru_2Rh^{103}}]^+ = 1602$, $[\mathrm{C_{48}H_{60}N_8S_4O_4Cl_{10}Ru_2Rh + H}]^+ = 1601$, $[\mathrm{C_{48}H_{60}\ N_8S_4O_4Cl_{10}Ru_2^{96}Rh}]^+ = 1590$, $[\mathrm{C_{32}H_{26}N_8 + H}]^+ = 523$.

2.2.2.4. *Preparation of* ***12***. Complex **12** was obtained from $[\mathrm{(dmso)_2H}]^+[trans\text{-}\mathrm{RhCl_4(dmso)_2}]^-$ [25], (0.2 mmol) in a manner similar to that used for synthesis of **9**. Color: Blackish-brown, Yield: 0.1244 g (83.8%); m.p. > 220°C; Found: C, 31.89; H, 3.85; N, 6.81; S, 11.70; $\mathrm{C_{44}H_{64}N_8S_6O_6Cl_{10}Rh_3}$ ($M_\tau = 1656$). Requires: C, 31.90; H, 3.89; N, 6.76; S, 11.61. Selected infrared absorption (KBr, $\mathrm{cm^{-1}}$): ν(N–H), 3439(w); ν(CH=N), 1618(s); ν(C=N), 1584(s); ν(SO), 1103(s), 1056(s); $\nu[\mathrm{(dmso)_2H}]^+$, 726(brs); ν(M–S), 406(m); ν(M–Cl), 358(s); ν(M–N), 276(s). Electronic spectra ($\lambda_{\max}$, nm (ε in $(\mathrm{mol\,L^{-1}})\,\mathrm{cm^{-1}}$)) in acetonitrile: 484(128), 408(298), 346(801), 297(1004). $\mu_{\mathrm{eff}} = 1.82\,\mu\mathrm{B}$; Δm at 25°C (Ω^{-1} in $(\mathrm{mol\,L^{-1}})\,\mathrm{cm^{-1}}$): 132 in DMSO. FAB-MS ($m/z$): $[\mathrm{C_{44}H_{64}N_8S_6O_6Cl_{10}^{37}Rh_3}]^+ = 1676$, $[\mathrm{C_{44}H_{64}N_8S_6O_6Cl_{10}Rh_3^{103}}]^+ = 1662$, $[\mathrm{C_{44}H_{64}N_8S_6O_6Cl_{10}Rh_3 + H}]^+ = 1657$, $[\mathrm{C_{32}H_{26}N_8 + H}]^+ = 523$.

3. Results and discussion

Empirical formulae of Schiff base (Schiff base ligand, SBL) and **1**–**12** were in conformity with elemental analyses. Molecular weights were determined by mass spectral study. In mass spectra of **1**–**12** isotopic patterns clearly identify Ru- and Rh-containing ions, because there are few relevant ions in spectrum. Only six important ions appear in each spectrum contain ruthenium, although there may be more than one kind of each of these ions due to the presence of different kinds of ligands in the analyte. Since ruthenium has six isotopes with significant natural abundance ($>15\%$) from 96 to 104 amu, rhodium has one 103 amu and Cl has two (35 and 37 amu). Metal complexes never give the parent ion in FAB-MS spectrum, as molecular ion (figure 1). Thus, the ion of highest mass observed in spectrum is the complex cation [26].

The molar conductivities for **1**–**7** were between 46 and 73 in DMSO, 98 and 113 in acetonitrile, and 138and 154 in acetone, within the ranges suggested for 1 : 1 electrolytes [27]. In solution one chloride is replaced by solvent, leading to the 1 : 1 electrolyte; the second chloride must not undergo exchange by another solvent molecule, or we would observe a 2 : 1 electrolyte.

To obtain qualitative information in relation to the type of species present in solution, **1** was analyzed by ESI-MS in acetonitrile. The ESI-MS method was chosen because ions formed upon ESI under soft ionization conditions correlate with species that exist in solution [28, 29]. The ESI-MS spectrum of **1** was recorded in different time intervals (initially to 48 h). The main peaks observed in ESI spectra were according to ion masses and their isotopic patterns Ru(II) gaseous mono-cations $[\mathrm{RuCl(SBL)(ACN)}]^+$ ($m/z = 700$) (figure 2). These findings are fully consistent with conductivity data, that during dissolution in solution, one chloride is replaced by solvent (reaction 1). However no further exchange with the second chloride is observed (reaction 2). Molar conductance for **8** was low, indicating its nonelectrolytic nature in solutions, confirming Cl^- remains coordinated. This feature also supports that rhodium derivatives, unlike the ruthenium complexes [30], are stable in solutions and have no

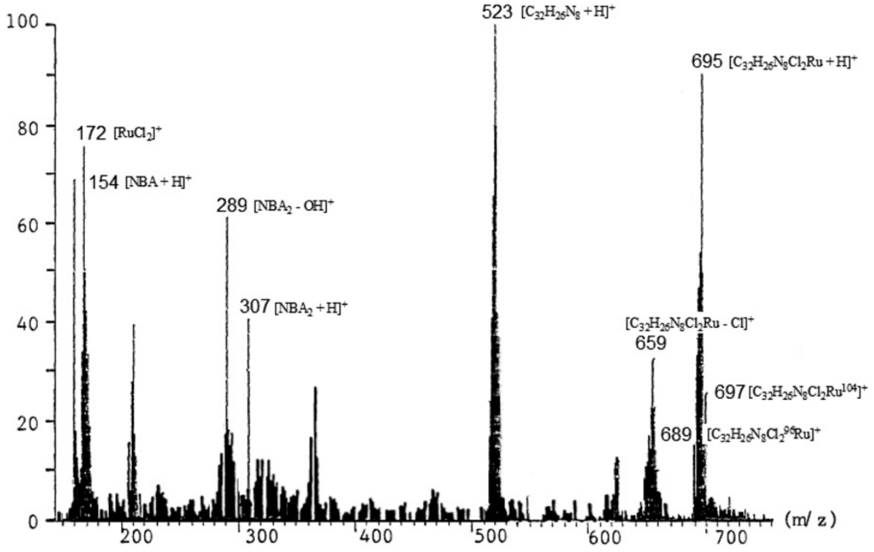


Figure 1. FAB-MS of **1**.

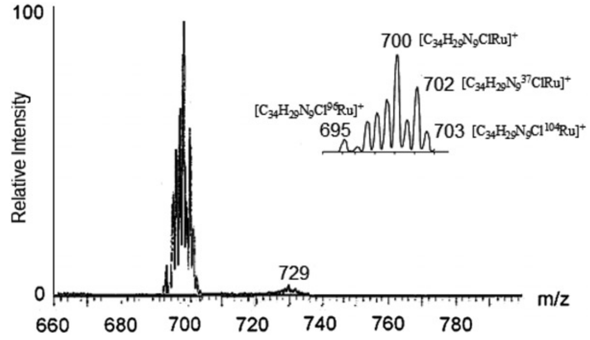


Figure 2. ESI-MS of **1** in acetonitrile.

tendency to form polymeric aggregates. Molar conductances for **9–12** were 118–138 indicating their ionic nature [24, 31].

$$[RuCl_2(SBL)] + Solvent \rightarrow [RuCl\,(SBL)(Solvent)]^+ + Cl^-, \qquad (1)$$

$$[RuCl(SBL)(Solvent)]^+ + Solvent \rightarrow \text{No exchange}. \qquad (2)$$

3.1. *Infrared spectral analysis*

In FTIR spectra of INH Schiff base, a band at 1690 cm^{-1}, corresponding to free (C=O) amide stretch [32], vanished in spectra of Schiff base chelate, suggesting complete condensation of amide C=O with primary amine. A new strong absorption at 1598 cm^{-1} is attributable to characteristic stretching frequencies of the imino linkage ν(C=N). The band for free ν(CH=N) in INH Schiff base, ~1635 cm^{-1}, is found at almost the same position in FTIR spectra of synthesized SBL. In complexes both bands were shifted to lower wavenumber by ~10–22 cm^{-1} indicating coordination takes place through the nitrogen of (C=N) group [33]. This was also confirmed by appearance of ν(M–N) at ~280 cm^{-1}. A weak band in the range ~3440 cm^{-1} in synthesized Schiff base is assigned for secondary –NH.

Pyridine ring vibrations are affected by nitrogen coordination with a metal. Most affected are pyridine ring deformation, in plane ring deformation, and out-of-plane deformation [34], which appear at 1580–1585, 620–640, and 410–420 cm^{-1}, respectively, in free ligands. In-plane ring deformation and out-of-plane deformation on coordination to metal show positive shifts by ~25–30 cm^{-1} [35, 36]. The pyridine ring deformation is less sensitive to coordination, in spectra of **2–7** and **9–12**; this band is superimposed or masked out. The $\nu(M–N_{py})$ at ~280 cm^{-1} also verified coordination of pyridine nitrogen with metal in these complexes [31].

In **2–7** and **9–12**, one or two bands at 1096–1128 cm^{-1} were assigned for ν(SO). This band at 1054 cm^{-1} for free dmso and 1028 cm^{-1} for free tmso shows a positive shift in ν(SO), indicating coordination of sulfur to metal. In all complexes a band near 400 cm^{-1} was assigned for ν(M–S). Sharp bands between 360 and 330 cm^{-1} were assigned for

ν(M–Cl) stretch. In **9**, **11**, and **12** a broad band at ~725 cm^{-1} along with a sharp band at ~1054 cm^{-1} for dmso analog and at 1028 cm^{-1} in tmso analog indicates the presence of hydrogen bonded dmso/tmso [20, 21, 24, 31].

3.2. *Electronic spectral analysis and magnetic moment*

Complexes **1**–**7** are diamagnetic (low spin d^6, $s = 0$), as expected for low spin Ru(II) and Rh(III) complexes. These complexes show four or five bands in electronic spectra. In **6** and **7**, three broad absorptions with low extinction coefficient were observed at 682–675 nm, 548–541 nm, and 407–404 nm, which may be assigned for $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$, and $^1A_{1g} \rightarrow {}^1T_{2g}$ of Rh(III) [37] and which may include $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transition assigned for Ru(II) complexes. In **1**–**5**, higher energy absorption at 420–402 nm was probably due to MLCT transition. However higher energy absorption bands below 340 nm were attributed to $\pi \rightarrow \pi^*$ intraligand transition in the coordinated π–acidic imine [38–41].

Low spin Ru(III) complexes are (d^5) and Rh(II) are (d^7) system. In electronic spectra of **9**–**11**, four bands were observed between 486 and 472 nm, 410 and 397 nm, 344 and 335 nm, and 303 and 299 nm. The intense absorption at ~406 nm coupled with a less intense transition at 480 nm was ascribed to charge transfer from chloride to Ru(III), a typical identification for $RuCl_4^-$ [42]. The lowest energy absorptions in **8**–**12** may correspond to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g} \rightarrow {}^4A_{2g}$, and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions of Rh(II). These bands are characteristic of an octahedral environment around Rh^{2+} [43]. In **9**, **11,** and **12** a weak absorption at 300 nm was due to the presence of protonated sulfoxide cation [38–41].

Complex **8** is paramagnetic with magnetic moment 1.87 BM. For **9**–**12**, magnetic moments range between 1.67 and 1.82 BM at room temperature, lower than the predicted values. This lowering may occur due to the presence of low symmetry ligand fields, metal–metal interactions, or extensive electron delocalization between the species linking paramagnetic centers [44]. This spin–spin alternation leads to antiferromagnetic coupling which depends on the number of atoms located between the interacting ions [45].

3.3. *NMR spectral analysis*

In ^{1}H-NMR spectrum of Schiff base, a sharp signal for two =N–NH groups was observed at δ 11.18 ppm [46], not much shifted after complexation, indicating noninvolvement of =N–NH in coordination. Nonappearance of signal for $-NH_2$ near δ 5.00 ppm indicates its involvement during condensation with (C=O) amide carbonyl. The singlet at δ 8.84 ppm was assigned for two azomethine protons. This signal shifts downfield between δ 9.18 and 9.02 ppm after complexation, probably due to lone pair donation from azomethine (CH=N) nitrogen to metal [47]. Signals for 22 aromatic and hetero aromatic protons were between δ 8.62 and 6.97 ppm.

In ^{1}H-^{1}H COSY NMR spectrum of Schiff base (Supplementary material), cross-peaks were observed in the aromatic region due to proton–proton coupling between connected carbons [20]. A signal for hetero aromatic proton at δ 8.62 ppm for $H_{py\text{-}ortho}$ is connected by cross-peak to the signal at δ 8.21 ppm assigned for $H_{py\text{-}meta}$. The signal Ar–H_{meta} at

δ 7.96 ppm is connected to two separate signals observed at δ 7.51 ppm for Ar–H_{para} and δ 6.97 ppm for Ar–H_{ortho} by cross-peaks.

In $^{13}C\{^1H\}$NMR spectra of Schiff base (Supplementary material), the multiplet between δ 133.6 and 122.8 ppm is assigned for aromatic carbons. Signal for (C=O) amide at δ 163.2 ppm in INH Schiff base spectra completely disappeared and a new signal was observed at δ 169.3 ppm, assigned for δ(C=N), confirming involvement of (C=O) amide in condensation. Signal for δ(CH=N) was observed at δ 168.6 ppm. Both signals were shifted downfield in all complexes, confirming binding of metal with imine nitrogen [47]. Thus on the basis of above discussion the most plausible structure for the ligand is suggested in figure 3.

In ^{1}H-NMR spectra of **1**–**7**, signals for aromatic protons were between δ 8.98 and 6.83 ppm and in $^{13}C\{^1H\}$-NMR spectra aromatic carbons were between δ 134.8 and 117.3 ppm.

In ^{1}H-NMR spectra of **2**, three singlets were observed with intensity 1 : 1 : 1, indicating three different methyl protons of dmso. Signals at δ 3.52 and δ 3.49 ppm (for 12 protons each) were assigned for CH_3 protons of dmso *trans* to Cl, which are diastereotopic; signal at δ 3.42 ppm was assigned for 12 methyl protons of dmso *trans* to pyridine of the chelate [20, 31, 48]. Similar structure is derived from $^{13}C\{^1H\}$-NMR spectra where three signals at δ 45.8, δ 44.9, and δ 43.6 ppm confirm the presence of three environments for methyl carbons.

In ^{1}H-NMR spectra of **3**, two singlets with intensity ratio 1 : 2 were observed, indicating two types of CH_3 protons. The singlet at δ 3.43 ppm for 12 protons was assigned for dmso *trans* to pyridine and the singlet at δ 3.32 ppm for 24 protons to dmso's *trans* to each other. In $^{13}C\{^1H\}$-NMR spectra two signals for (S–C) carbon of dmso at δ 45.3 and δ 44.6 ppm confirms the ^{1}H suggestions.

However in ^{1}H-NMR spectra of **4**, four signals were observed with relative intensity of 1 : 1 : 1 : 3, indicating four environments for tmso protons. Multiplets at δ 4.06 and δ 4.01 ppm (for eight protons each) are assigned for S–CH_2 of tmso, *trans* to Cl, and probably diastereotopic. The multiplet centered at δ 3.51 ppm, for eight protons, was assigned for two S–CH_2 protons of tmso *trans* to pyridine of the chelate. The multiplet at δ 2.31 ppm was assigned for 24 protons of all S–C–CH_2 groups [31, 48–50].

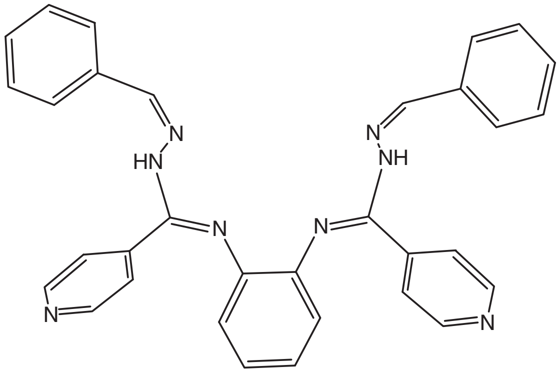


Figure 3. 3-D structure of Schiff base.

Similarly in $^{13}C\{^1H\}$-NMR spectra of this complex signals at δ 57.8 and δ 57.4 ppm were assigned for S–C of tmso *trans* to Cl and signal at δ 55.9 ppm for S–C of tmso *trans* to pyridine. Signals at δ 27.3, δ 26.8, and δ 25.1 ppm were assigned for (S–C–C) carbons of tmso.

Similarly, **5** exhibits three sets of multiplets centered at δ 3.98, δ 3.53, and δ 3.36 ppm. Signals at δ 3.98 and δ 3.53 ppm were assigned for S–CH_2 and the signal at δ 3.36 ppm for S–C–CH_2 of tmso. Intensity ratio of these three signals is 1 : 2 : 3. Thus one tmso is *trans* to the nitrogen and the other two are *trans* to each other. Similar conclusion can be inferred from $^{13}C\{^1H\}$-NMR spectra, where signals are observed at δ 57.2 ppm (S–C *trans* to pyridine nitrogen) and δ 55.8 ppm (S–C tmso *trans* to each other). Signals at δ 27.0 and δ 25.4 ppm are for (S–C–C) carbon of tmso [31, 48–50].

In ^1H-NMR spectra of **6**, two singlets with intensity 1 : 1 indicate two different types of protons; δ 3.48 ppm for 12 protons was assigned for methyl of dmso *trans* to Cl and δ 3.36 ppm was assigned for 12 methyl protons of dmso *trans* to pyridine. In $^{13}C\{^1H\}$-NMR spectra two signals were observed for S–C of dmso at δ 45.7 and δ 44.8 ppm [31, 48].

In ^1H-NMR spectra of **7**, three multiplets were observed. Signals at δ 3.96 and δ 3.68 ppm were assigned for S–CH_2 and at δ 2.48 ppm for S–C–CH_2 of tmso [31, 48–50]. In $^{13}C\{^1H\}$-NMR spectra, δ 57.6 ppm was assigned for S-C of tmso *trans* to Cl and δ 56.2 ppm for S–C of tmso *trans* to pyridine. Signals at δ 26.9 and δ 25.3 ppm were assigned for S–C–C of tmso.

3.4. *Thermal analysis*

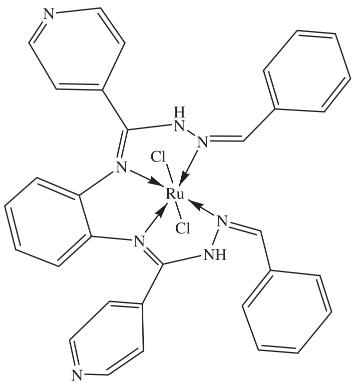
Thermal analysis gives information about stability of metal chelates and water molecules inside or outside the coordination sphere. In **1** and **8**, decomposition involved two steps, the first step loss of two chlorides at 280–300°C and the second loss at 350–450°C, giving M_2O_3 [M = Ru(II) and Rh(II)]. The end products of stable metal oxides such as Ru_2O_3, Rh_2O_3 and sometimes even RuO_2 were found at 680–720°C as matter [36, 51]. The absence of an endothermic peak confirmed that the complexes were not hydrated.

3.5. *Structures of 1–7*

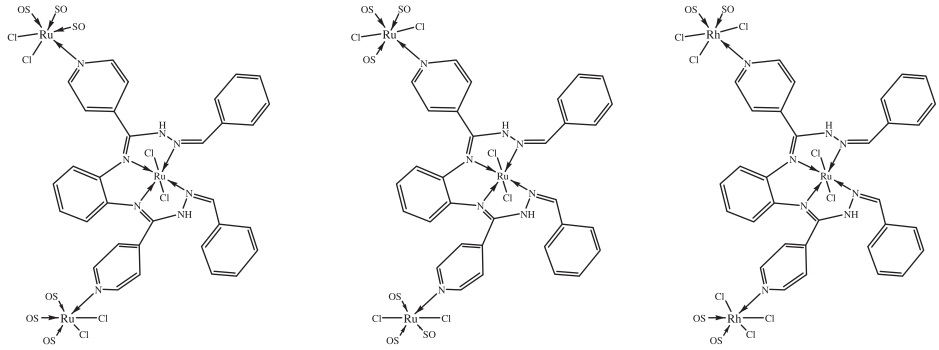
On the basis of elemental analyses, conductivity experiments, TGA, and spectroscopic studies (FTIR, UV-Vis, FAB-mass, ESI-MS, ^1H-NMR, and $^{13}C\{^1H\}$-NMR) the most plausible structures for **1**–**7** are suggested in figure 4.

3.6. *Structure of paramagnetic complexes 8–12*

Signals in NMR spectra of **8**–**12** were broad and shifted from their original position, due to paramagnetism [31, 47, 48]. Aqueous solution of **8** does not respond to qualitative silver nitrate test, confirming that rhodium is +2 and no Cl^- ion is coupled through primary valence to central metal ion. The binding modes of chelate in **8**–**12** are



Complex **1**



Complex **2/4** Complex **3/5** Complex **6/7**

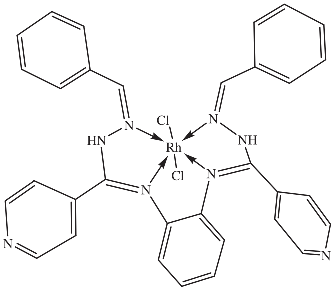
SO = dmso in **2, 3, 6** and tmso in **4, 5, 7**

Figure 4. 3-D structure of **1**–**7**.

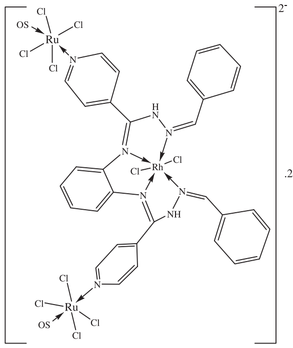
concluded on the basis of elemental analyses, conductivity experiments, TGA, and spectroscopic (FTIR, UV-Vis, and FAB-mass) studies as suggested in figure 5.

4. Conclusion

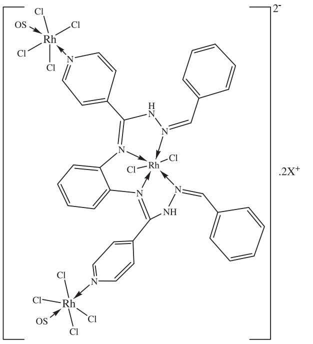
We have prepared and spectroscopically characterized two Ru^{II}/Rh^{II} complexes with a new *bis*-*N*,*N*′-bidentate Schiff base. This Ru^{II}/Rh^{II} Schiff base complex was utilized as spacer in stepwise synthesis of trinuclear compounds. Participation of passive amide carbonyl group in Schiff base condensation makes synthesis of the ligand quite interesting. The imine interactions with metal and lone pair donation from metal chelate to sulfoxide precursors make syntheses fascinating. Consequently, tailored synthetic approach plays a significant role in the preparation of multi-nuclear



Complex **8**



Complex **9/10/11**



Complex **12**

SO = dmso in **9, 10, 12** and tmso in **11**.
$[X]^+ = [(dmso)_2H]^+$ in **9** and **12;** $[Na]^+$ in 10; $[(tmso)H]^+$ in **11**.

Figure 5. 3-D structure of **8–12**.

compounds. Qualitative examination of Ru^{II}/Rh^{II} Schiff base chelate complexes in solutions conclude that on dissolution, in the Ru^{II} complex one chloride is substituted with solvent, resulting in 1 : 1 electrolyte, while Rh^{II} chelate complexes are stable in solutions.

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