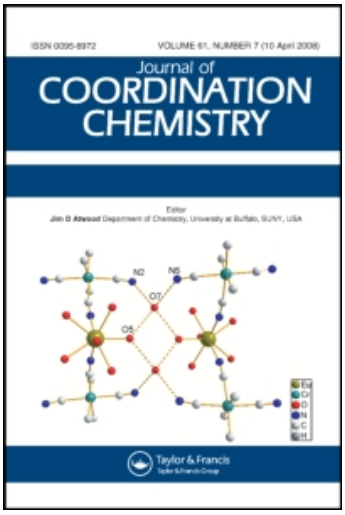

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Tailored synthesis, spectroscopic, catalytic, and antibacterial studies of dinuclear ruthenium (II/III) chloro sulfoxide complexes with *5-nitro-o*-phenanthroline as a spacer

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Tailored synthesis, spectroscopic, catalytic, and antibacterial studies of dinuclear ruthenium (II/III) chloro sulfoxide complexes with *5-nitro-o*-phenanthroline as a spacer

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A dinucleating spacer incorporating *o*-phenanthroline has been synthesized and characterized. The reaction of this spacer with ruthenium precursors resulted in formation of dinuclear complexes, [*cis*,*fac*-$RuCl_2(SO)_3$ (μ-*nphen*)*cis*,*cis*-$RuCl_2(SO)_2$], [*trans*,*mer*-$RuCl_2(SO)_3$ (μ-*nphen*)*trans*, *cis*-$RuCl_2(SO)_2$], and $[X]^+[$*trans*-$RuCl_4(SO)$(μ-*nphen*)*mer*-$RuCl_3(SO)]^-$, where SO = dimethylsulfoxide/tetramethylenesulfoxide, *nphen* = *5-nitro-o*-phenanthroline, and $X^+ = [(dmso)_2H]^+$, Na^+, and $[(tmso)H]^+$. These complexes were characterized by elemental analyses, conductivity measurements, magnetic susceptibility, FT-IR, FAB-Mass, ^{1}H-NMR, $^{13}C\{^1H\}$-NMR, and electronic spectroscopy. [trans,mer-$RuCl_2$(dmso)3(μ-nphen)trans,cis-$RuCl_2(dmso)_2$] was also characterized on the basis of ^1H–^1H COSY NMR. The coordination of one ruthenium is through heterocyclic nitrogen of the *o*-phenanthroline and the second is through the oxygen of the nitrito group. Catalytic activity of these complexes has been investigated in hydrolysis of benzonitrile. All the complexes possess antibacterial activity against *Escherichia coli* and are compared to Chloramphenicol.

Keywords: Ruthenium; Spacer; Dimethylsulfoxide; Tetramethylenesulfoxide; *5-Nitro-o*-phenanthroline

1. Introduction

Antitumor and antimetastatic activity of several ruthenium complexes has generated interest in synthesis of new ruthenium compounds with potential as anticancer agents [1–12]. Dinuclear ruthenium complexes have advantages [13–16] over mononuclear analogues because of increased size and higher metal percentage.

Two rutheniums bonded by a bidentate heterocyclic ligand provide remarkable stability and potential therapeutic uses. Polynuclear ruthenium complexes of *o*-phenanthroline are currently being investigated because of rich electrochemical and photophysical properties and potential application in supramolecular structures.

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These systems can be synthesized by covalent linking of building block with designed spacers [17, 18]. We were interested in developing a bimetallic system with a heteroaromatic spacer and have synthesized *5-nitro-o*-phenanthroline and prepared seven dinuclear ruthenium complexes with this spacer.

2. Experimental

The $RuCl_3 \cdot 3H_2O$ (E.Merck), *o*-phenanthroline monohydrate (E.Merck), tetramethylenesulfoxide (Lancaster, UK), Muller Hinton Agar Media (Himedia), and sodium hydroxide (E.Merck) were used as received. Analytical grade dimethylsulfoxide (E.Merck), nitric acid (E.Merck), sulfuric acid (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. FT-IR spectra were recorded in KBr pellets on a Shimadzu-8400 PC, FT-IR spectrophotometer. ^{1}H-NMR and $^{13}C\{^1H\}$-NMR spectra were recorded in D_2O on a Bruker DRX-300 NMR spectrometer. Guoy's method was employed for measurement of magnetic susceptibility. Cobalt mercurytetrathiocyanate was used as standard. Diamagnetic correction was made by using Pascal's constants. Elemental analyses (C, H, and N) were performed on an Elementra Vario EL III, Elemental analyzer. FAB-Mass spectra were recorded on a Jeol SX-102 Mass spectrometer. ^1H–^1H COSY NMR was recorded in D_2O on a Bruker Avance-400 NMR spectrometer.

3. Synthesis of ligand

3.1. *Synthesis of 5-nitro-o-phenanthroline [19]*

To a solution of *o*-phenanthroline (1 g, 5.04 mmol) in concentrated sulfuric acid (10 mL), a mixture of fuming nitric acid (2 mL) and concentrated sulfuric acid (2 mL) was added and the reaction mixture heated at 100°C for 2 h. Resulting mixture was diluted with water and made basic with sodium hydroxide. Light brown solid precipitated, was filtered, washed with water, dried, and recrystallized from ethanol as colorless needles. Yield: 0.9634 g (84.8%); m.p. = 200°C; Found: C, 63.9; H, 2.9; N, 18.5; $C_{12}H_7N_3O_2$ ($M_\tau = 225$). Requires: C, 64.0; H, 3.1; N, 18.7. Selected infrared absorption (KBr, cm^{-1}): ν(Ar−H), 3387(s), 3269(s), 3040(s); ν(C=C) + (C=N), 1608(s), 1542(s), 1438(s); νNO_2, 1300(s), 1262(s); δ(Ar−H), 766(s); $\rho(NO_2)$, 634(s).

4. Synthesis of complexes

4.1. *Synthesis of [*cis, fac-*$RuCl_2(dmso)_3$ (*μ-5-nitro-o-*phenanthroline)*cis, cis-*$RuCl_2(dmso)_2$] (1)*

The precursor complex [*cis*, *fac*-$RuCl_2$(S-dmso)$_3$(O-dmso)] was prepared according to literature procedure [20]. Recrystallized [*cis*,*fac*-$RuCl_2$(S-dmso)$_3$(O-dmso)]

(0.030 g, 0.06 mmol) was dissolved in 0.2 mL of dmso in a two-neck flask. The ligand *5-nitro-o*-phenanthroline (0.0139 g, 0.06 mmol) dissolved in 7 mL acetone was added to the reaction mixture and stirred for 2 h. The reaction solution changes yellow to red yellow. To this solution [*cis*,*fac*-$RuCl_2$(S-dmso)$_3$(O-dmso)], (0.030 g, 0.06 mmol) dissolved in 0.2 mL dmso, was added and the reaction mixture was kept under reflux for 4 h in an inert atmosphere. The reaction mixture changes from red yellow to deep red. Decanting the transparent deep red solution, it was evaporated under vacuum and after 2 days red micro crystals were observed, collected and washed with acetone/diethyl ether (1 : 1) solvent mixture. Yield: 0.0482 g (81.0%); m.p. = 127°C; Found: C, 27.54; H, 3.88; N, 4.39; S, 16.72; $C_{22}H_{37}N_3S_5O_7Cl_4Ru_2$ ($M_\tau = 959$). Requires: C, 27.53; H, 3.89; N, 4.38; S, 16.70. Selected infrared absorption (KBr, cm^{-1}): ν(C=C) + (C=N), 1631(s), 1600(s), 1585(w), 1517(s); νSO, 1106(s); δ(ONO), 824(s); ν(M−O), 503(s); ν(Ru−S), 402(m); ν(Ru−Cl), 339(s), 332(sh); ν(Ru−N), 281(s). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 680(81), 542(102), 411(462), 298(846). Δm at 25°C (Ω^{-1} in $M^{-1}\,cm^{-1}$): 69 in water; ^{1}H-NMR (300 MHz, δ, D_2O): 8.34 (d, 1H, H_9 *5-nitro-o-phen*), 8.32 (d, 1H, H_2 *5-nitro-o-phen*), 7.86 (s, 1H, H_6 *5-nitro-o-phen*), 7.82 (d, 1H, H_7 *5-nitro-o-phen*), 7.79 (d, 1H, H_4 *5-nitro-o-phen*), 6.91 (dd, 1H, H_8 *5-nitro-o-phen*), 6.86 (dd, 1H, H_3 *5-nitro-o-phen*), 3.62 (s, 6H, CH_3), 3.43 (s, 12H, CH_3), 3.29 (s, 6H, CH_3), 3.03 (s, 6H, CH_3); $^{13}C\{^1H\}$-NMR (300 MHz, δ, D_2O): 160.9 (C_9 *5-nitro-o-phen*), 159.1 (C_2 *5-nitro-o-phen*), 148.9 ($C_{10'}$ *5-nitro-o-phen*), 148.6 ($C_{1'}$ *5-nitro-o-phen*), 148.1 (C_5 *5-nitro-o-phen*), 143.9 (C_7 *5-nitro-o-phen*), 138.5 (C_4 *5-nitro-o-phen*), 130.3 (C_8 *5-nitro-o-phen*), 130.2 (C_3 *5-nitro-o-phen*), 130.1 ($C_{6'}$ *5-nitro-o-phen*), 129.9 (C_6 *5-nitro-o-phen*), 127.4 ($C_{4'}$ *5-nitro-o-phen*), 45.9 (S–C), 44.8 (S–C), 44.2 (S–C), 42.6 (S–C). FAB-MS $[M + H]^+$ $m/z = 960$.

4.2. *Synthesis of* [trans, mer-*$RuCl_2$(dmso)$_3$*(μ-5-nitro-o-*phenanthroline*)trans, cis-*$RuCl_2$(dmso)$_2$*] (2)

The precursor [*trans*-$RuCl_2$(dmso)$_4$] was prepared according to literature procedure [4]. Recrystallized [*trans*-$RuCl_2$(dmso)$_4$] (0.030 g, 0.06 mmol) was dissolved in 0.2 mL of dmso in a two-neck flask and *5-nitro-o*-phenanthroline (0.0139 g, 0.06 mmol) dissolved in 8 mL of acetone was added to the reaction mixture and stirred for 2 h. The reaction solution changes from pale yellow to orange. To this solution [*trans*-$RuCl_2$(dmso)$_4$] (0.030 g, 0.06 mmol), dissolved in 0.2 mL dmso, was added and kept under reflux for 5 h in an inert atmosphere. Color of the reaction solution changes from light orange to red orange. Decanted transparent red orange solution was evaporated under vacuum. Orange red micro crystals were formed after 1 day, collected and washed several times with acetone/diethyl ether (1 : 1) solvent mixture. Yield: 0.0520 g (87.4%). m.p. = 142°C); Found: C, 27.55; H, 3.87; N, 4.37; S, 16.71; $C_{22}H_{37}N_3S_5O_7Cl_4Ru_2$ ($M_\tau = 959$). Requires: C, 27.53; H, 3.89; N, 4.38; S, 16.70. Selected infrared absorption (KBr, cm^{-1}): ν(C=C) + (C=N), 1628(s), 1604(sh), 1572(s), 1524(s); νSO, 1099(s); δ(ONO), 824(s); ν(M−O), 531(s); ν(Ru−S), 401(m); ν(Ru−Cl), 335(s), 328(sh); ν(Ru−N), 276(s). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 657(64), 548(96), 407(509), 294(798). Δm at 25°C (Ω^{-1} in $M^{-1}\,cm^{-1}$): 56 in water; ^{1}H-NMR (300 MHz, δ, D_2O): 8.37 (d, 1H, H_9 *5-nitro-o-phen*), 8.28 (d, 1H, H_2 *5-nitro-o-phen*), 7.97 (s, 1H, H_6 *5-nitro-o-phen*), 7.83 (d, 1H, H_7 *5-nitro-o-phen*), 7.80 (d, 1H, H_4 *5-nitro-o-phen*), 6.97 (dd, 1H, H_8 *5-nitro-o-phen*), 6.89 (dd, 1H, H_3 *5-nitro-o-phen*),

3.27 (s, 6H, CH_3), 3.08 (s, 12H, CH_3), 3.05 (s, 12H, CH_3); $^{13}C\{^1H\}$-NMR (300 MHz, δ, D_2O): 160.9 (C_9 *5-nitro-o-phen*), 159.5 (C_2 *5-nitro-o-phen*), 148.6 ($C_{10'}$ *5-nitro-o-phen*), 148.4 ($C_{1'}$ *5-nitro-o-phen*), 148.1 (C_5 *5-nitro-o-phen*), 143.6 (C_7 *5-nitro-o-phen*), 138.3 (C_4 *5-nitro-o-phen*), 130.1 (C_8 *5-nitro-o-phen*), 130.0 (C_3 *5-nitro-o-phen*), 130.2 ($C_{6'}$ *5-nitro-o-phen*), 129.6 (C_6 *5-nitro-o-phen*), 127.8 ($C_{4'}$ *5-nitro-o-phen*), 44.7 (S–C), 42.9 (S–C), 42.1 (S–C). FAB-MS $[M+H]^+$ $m/z = 960$.

4.3. *Synthesis of [(dmso)$_2$H]$^+$[*trans*-RuCl$_4$(dmso)(μ-5-nitro-o-phenanthroline) *mer*-RuCl$_3$(dmso)]$^-$ (3)*

The precursor $[(dmso)_2H]^+[trans\text{-}RuCl_4(dmso)_2]^-$ was prepared according to procedure given by Alessio *et al.* [5]. Recrystallized $[(dmso)_2H]^+[trans\text{-}RuCl_4(dmso)_2]^-$ (0.040 g, 0.07 mmol) was dissolved in 0.2 mL of dmso in a two-neck flask; *5-nitro-o*-phenanthroline (0.0162 g, 0.07 mmol) dissolved in 9 mL of acetone was added to the reaction mixture and stirred for 2 h with color change from red orange to light orange. To this solution $[(dmso)_2H]^+[trans\text{-}RuCl_4(dmso)_2]^-$ (0.040 g, 0.07 mmol), dissolved in 0.2 mL of dmso, was added and refluxed for 4 h in inert atmosphere. Color changed from light orange to yellow orange. After decanting, the transparent yellowish orange solution was evaporated under vacuum to yield a yellow orange solid which was washed several times with acetone/diethyl ether (1 : 1). Yield: 0.0584 g (82.1%); m.p. = 180°C); Found: C, 24.28; H, 3.27; N, 4.24; S, 12.96; $C_{20}H_{32}N_3S_4O_6Cl_7Ru_2$ ($M_\tau = 989$). Requires: C, 24.29; H, 3.26; N, 4.25; S, 12.97. Selected infrared absorption (KBr, cm^{-1}): ν(C=C) + (C=N), 1624(s), 1597(sh), 1528(s), 1498(sh); νSO, 1096(s),1054(s); δ(ONO), 831(s); ν(M–O), 522(s); ν(Ru–S), 403(m); ν(Ru–Cl), 336(s), 328(sh); ν(Ru–N), 273(s); $\nu[(dmso)_2H]^+$, 724(brs). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 609(72), 486(110), 406(512), 298(822). $\mu_{eff} = 1.86\,\mu B$, Δm at 25°C (Ω^{-1} in $M^{-1}\,cm^{-1}$): 108 in water. FAB-MS $[M+H]^+$ $m/z = 990$.

4.4. *Synthesis of [Na]$^+$[*trans*-RuCl$_4$(dmso)(μ-5-nitro-o-phenanthroline) *mer*-RuCl$_3$(dmso)]$^-$ (4)*

The precursor $(Na)^+[trans\text{-}RuCl_4(dmso)_2]^-$ was prepared according to literature procedure [5]. Recrystallized $(Na)^+[trans\text{-}RuCl_4(dmso)_2]^-$ (0.045 g, 0.106 mmol) was dissolved in 0.3 mL of dmso in a two-neck flask and *5-nitro-o*-phenanthroline (0.0239 g, 0.106 mmol) dissolved in 11 mL of acetone was added and stirred for 2 h. Orange reaction mixture became light. To this solution $(Na)^+[trans\text{-}RuCl_4(dmso)_2]^-$ (0.045 g, 0.106 mmol), dissolved in 0.3 mL of dmso was added and refluxed for 5 h with change from orange to yellow orange. Decanted yellowish orange transparent solution was evaporated under vacuum and the product washed several times with acetone/diethyl ether (1: 1). Yield: 0.0764 g (84.0%); m.p. = 151°C; Found: C, 22.50; H, 2.25; N, 4.91; S, 7.51; $C_{16}H_{19}N_3S_2O_4Cl_7NaRu_2$ ($M_\tau = 854$). Requires: C, 22.48; H, 2.24; N, 4.92; S, 7.50. Selected infrared absorption (KBr, cm^{-1}): ν(C=C) + (C=N), 1654(sh), 1603(s), 1580(s), 1514(s); νSO, 1106(s); δ(ONO), 817(s); ν(M–O), 551(s); ν(Ru–S), 397(m); ν(Ru–Cl), 330(s), 324(sh); ν(Ru–N), 273(s). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 603(46), 478(117), 396(542), 300(789). $\mu_{eff} = 1.84\,\mu B$, Δm at 25°C (Ω^{-1} in $M^{-1}\,cm^{-1}$): 122 in water. FAB-MS $[M+Na]^+$ $m/z = 877$.

4.5. *Synthesis of* [cis, fac-*RuCl$_2$(tmso)$_3$*(μ-5-nitro-o-*phenanthroline)*cis, cis-*RuCl$_2$(tmso)$_2$*] (5)

The precursor [*cis*-$RuCl_2(tmso)_4$], prepared from recrystallized [*cis*, *fac*-$RuCl_2(S\text{-}dmso)_3(O\text{-}dmso)$], according to literature procedure [21] (0.060 g, 0.102 mmol), was dissolved in 0.3 mL of tmso in a two-neck flask. *5-nitro-o*-phenanthroline (0.023 g, 0.102 mmol) dissolved in 8 mL of acetone was added to the reaction mixture and stirred for 2 h; the color changed from pale yellow to red. To this solution [*cis*-$RuCl_2(tmso)_4$], (0.060 g, 0.102 mmol), dissolved in 0.3 mL of tmso, was added and refluxed for 6 h with change to maroon. Decanted maroon solution was evaporated under vacuum to yield dark red solid which was washed several times with acetone/diethyl ether (1 : 1). Yield: 0.0964 g (86.8%); m.p. $>250^\circ$C; Found: C, 35.25; H, 4.34; N, 3.86; S, 14.70; $C_{32}H_{47}N_3S_5O_7Cl_4Ru_2$ ($M_\tau = 1090$). Requires: C, 35.26; H, 4.35; N, 3.85; S, 14.71. Selected infrared absorption (KBr, cm^{-1}): ν(C=C) + (C=N), 1643(s), 1559(sh), 1547(s), 1468(s), 1452(s); νSO, 1128(s); δ(ONO), 837(s); ν(M–O), 554(s); ν(Ru–S), 406(m); ν(Ru–Cl), 331(s), 329(sh); ν(Ru–N), 277(s). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 642(57), 532(106), 421(489), 301(803). Δm at 25°C (Ω^{-1} in $M^{-1}\,cm^{-1}$): 65 in water; ^{1}H–NMR (300 MHz, δ, D_2O): 8.28 (d, 1H, H_9 *5-nitro-o-phen*), 8.25 (d, 1H, H_2 *5-nitro-o-phen*), 7.94 (s, 1H, H_6 *5-nitro-o-phen*), 7.90 (d, 1H, H_7 *5-nitro-o-phen*), 7.87 (d, 1H, H_4 *5-nitro-o-phen*), 6.93 (dd, 1H, H_8 *5-nitro-o-phen*), 6.88 (dd, 1H, H_3 *5-nitro-o-phen*); 4.18 (m, 4H, S–CH_2), 4.03 (m, 4H, S–CH_2), 3.98 (m, 8H, S–CH_2), 3.44 (m, 4H, S–CH_2), 2.32(m, 20H, S–C–CH_2); $^{13}C\{^1H\}$-NMR (300 MHz, δ, D_2O): 159.4(C_9 *5-nitro-o-phen*), 159.0 (C_2 *5-nitro-o-phen*), 148.3 ($C_{10'}$ *5-nitro-o-phen*), 148.1 ($C_{1'}$ *5-nitro-o-phen*), 147.9 (C_5 *5-nitro-o-phen*), 143.4 (C_7 *5-nitro-o-phen*), 138.6 (C_4 *5-nitro-o-phen*), 130.3 (C_8 *5-nitro-o-phen*), 130.2 (C_3 *5-nitro-o-phen*), 130.1 ($C_{6'}$ *5-nitro-o-phen*), 129.3 (C_6 *5-nitro-o-phen*), 127.6 ($C_{4'}$ *5-nitro-o-phen*), 57.9 (S–C), 54.7 (S–C), 54.1 (S–C), 53.1 (S–C); 27.4 (S–C–C), 26.8 (S–C–C), 26.3 (S–C–C), 24.1 (S–C–C). FAB-MS $[M + H]^+$ $m/z = 1091$.

4.6. *Synthesis of* [trans, *mer*-*RuCl$_2$(tmso)$_3$*(μ-5-nitro-o-*phenanthroline)*trans, cis-*RuCl$_2$(tmso)$_2$*] (6)

The precursor [*trans*-$RuCl_2(tmso)_4$] was prepared from recrystallized [*trans*-$RuCl_2(dmso)_4$] [21] and recrystallized [*trans*-$RuCl_2(tmso)_4$] (0.035 g, 0.059 mmol) was dissolved in 0.2 mL of tmso in a two-neck flask. The *5-nitro-o*-phenanthroline (0.0134 g, 0.059 mmol) dissolved in 9 mL of acetone was added and stirred for 2 h with color change from light yellow to orange. To this solution [*trans*-$RuCl_2(tmso)_4$] (0.035 g, 0.059 mmol), dissolved in 0.2 mL of tmso, was added and refluxed for 7 h, changing to red orange. Decanted transparent red orange solution was evaporated under vacuum, to yield red orange solid. It was washed several times with acetone/diethyl ether (1 : 1). Yield: 0.0582 g (89.8%); m.p. = 118°C; Found: C, 35.27; H, 4.36; N, 3.87; S, 14.72; $C_{32}H_{47}N_3S_5O_7Cl_4Ru_2$ ($M_\tau = 1090$). Requires: C, 35.26; H, 4.35; N, 3.85; S, 14.71. Selected infrared absorption (KBr, cm^{-1}): ν(C=C) + (C=N), 1643(s), 1639(sh), 1601(s), 1527(s), 1459(s); νSO, 1127(s); δ(ONO), 833(s); ν(M–O), 562(s); ν(Ru–S), 402(m); ν(Ru–Cl), 333(s), 337(sh); ν(Ru–N), 271(s). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 663(48), 528(89), 419(494), 300(822). Δm at 25°C (Ω^{-1} in $M^{-1}\,cm^{-1}$): 63 in water; ^{1}H-NMR (300 MHz, δ, D_2O): 8.32 (d, 1H, H_9

5-nitro-o-phen), 8.29 (d, 1H, H_2 *5-nitro-o-phen*), 7.76 (s, 1H, H_6 *5-nitro-o-phen*), 7.82 (d, 1H, H_7 *5-nitro-o-phen*), 7.84 (d, 1H, H_4 *5-nitro-o-phen*), 6.88 (dd, 1H, H_8 *5-nitro-o-phen*), 6.79 (dd, 1H, H_3 *5-nitro-o-phen*), 4.01 (m, 4H, S–CH_2), 3.53 (m, 8H, S–CH_2), 3.42 (m, 8H, S–CH_2), 3.35 (m, 20H, S–C–CH_2); $^{13}C\{^1H\}$-NMR (300 MHz, δ, D_2O): 160.7 (C_9 *5-nitro-o-phen*), 159.1 (C_2 *5-nitro-o-phen*), 148.7 ($C_{10'}$ *5-nitro-o-phen*), 148.3 ($C_{1'}$ *5-nitro-o-phen*), 147.9 (C_5 *5-nitro-o-phen*), 143.9 (C_7 *5-nitro-o-phen*), 138.3 (C_4 *5-nitro-o-phen*), 130.8 (C_8 *5-nitro-o-phen*), 130.4 (C_3 *5-nitro-o-phen*), 130.1 ($C_{6'}$ *5-nitro-o-phen*), 129.2 (C_6 *5-nitro-o-phen*), 127.5 ($C_{4'}$ *5-nitro-o-phen*), 54.1 (S–C), 53.9 (S–C), 53.3 (S–C), 26.1 (S–C–C), 23.9 (S–C–C), 23.1 (S–C–C). FAB-MS $[M+H]^+$ $m/z = 1091$.

4.7. *Synthesis of [H(tmso)]$^+$[trans-RuCl$_4$(tmso)(μ-5-nitro-o-phenanthroline) mer-RuCl$_3$(tmso)]$^-$ (7)*

The precursor $[(tmso)H]^+[trans\text{-}RuCl_4(tmso)_2]^-$, prepared according to literature procedure [21], (0.0375 g, 0.067 mmol), was dissolved in 0.2 mL of tmso in a two-neck flask; *5-nitro-o*-phenanthroline (0.0152 g, 0.067 mmol) dissolved in 11 mL of acetone was added to the reaction mixture and stirred for 2 h changing from orange red to red. To this solution $[(tmso)H]^+[trans\text{-}RuCl_4(tmso)_2]^-$ (0.0375 g, 0.067 mmol), dissolved in 0.2 mL of tmso, was added and refluxed for 4 h changing to dark maroon. Decanted solution was evaporated under vacuum and after three days dark red micro crystals formed, were collected and washed with acetone/diethyl ether, (1 : 1). Yield: 0.0593 g (88.9%); m.p. = 154°C; Found: C, 29.14; H, 3.27; N, 4.24; S, 9.72; $C_{24}H_{23}N_3S_3O_5Cl_7Ru_2$ ($M_\tau = 989$). Requires: C, 29.15; H, 3.26; N, 4.25; S, 9.73. Selected infrared absorption (KBr, cm^{-1}): ν(C=C) + (C=N), 1630(s), 1598(sh), 1587(sh), 1532(s), 1446(s); νSO, 1126(s), 1028(s); δ(ONO), 831(s); ν(M–O), 591(s); ν(Ru–S), 406(m); ν(Ru–Cl), 335(s), 338(sh); ν(Ru–N), 277(s); $\nu[(tmso)H]^+$, 739(brs). Electronic spectra (λ_{max}, nm (ε in $M^{-1}\,cm^{-1}$)) in acetonitrile: 623(63), 472(109), 401(498), 301(806). $\mu_{eff} = 1.89\,\mu B$, Δm at 25°C (Ω^{-1} in $M^{-1}\,cm^{-1}$): 138 in water. FAB-MS $[M+H]^+$ $m/z = 990$.

5. Results and discussion

Empirical formulas of **1–7** were in conformity with elemental analyses. Molecular weights of the complexes were determined by FAB-Mass spectra, where molecular ion peaks were observed. The conductance of **1**, **2**, **5**, and **6** were low in water indicating non-electrolytes. Molar conductance of **3**, **4**, and **7** were comparatively higher indicating their ionic nature.

Complexes **1**, **2**, **5**, and **6** were diamagnetic (low spin d^6, $s = 0$), as expected for low spin Ru(II) complexes. These complexes show four bands in electronic spectra, two weak absorption bands between 680–642 nm and 548–528 nm due to d–d transitions ($^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$, respectively) and higher energy absorption at 421–407 nm due to MLCT transition. The other higher energy absorption bands below 300 nm are attributed to $\pi \rightarrow \pi^*$ intraligand transition in the coordinated π-acidic imine [22–25].

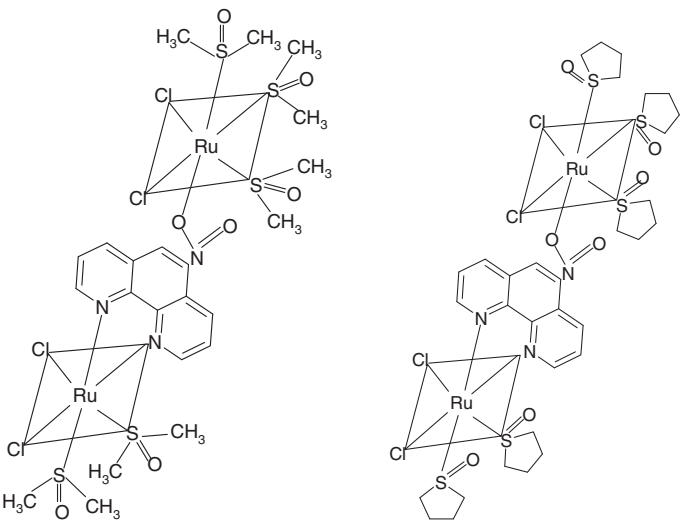
Complexes **3**, **4**, and **7** were paramagnetic with magnetic moments between 1.84 and 1.89 BM, as expected for low spin (d^5) Ru(III) complexes. Electronic spectra of these complexes show four bands in the ranges 623–603 nm, 486–472 nm, 406–396 nm, and 300–298 nm. The band between 623–603 nm has low extinction coefficient. The intense absorption at ~406 nm, coupled with a less intense transition at 470 nm, was ascribed to charge transfer from chloride to Ru(III), typical for $RuCl_4^-$ [26]. In **3** and **7** a weak absorption at about 300 nm was probably due to protonated sulfoxide [22–25].

In FT-IR spectra, three sharp absorptions for the cyclic C=C and C=N were observed at 1608, 1542, and 1438 cm^{-1} in the free ligand [27]. In the complexes a positive shift was observed in each signal by 40–45 cm^{-1}, indicating involvement of cyclic nitrogen in coordination [28], confirmed by appearance of ν(Ru–N) at ~280 cm^{-1}. In spectra of free ligand two sharp stretching bands for $\nu_{as}(NO_2)$ and $\nu_s(NO_2)$ were observed at 1300 and 1262 cm^{-1}, respectively, and a sharp band was observed at 620 cm^{-1} assigned for the wagging mode $\rho(NO_2)$, which disappeared in spectra of the complexes [29], due to transformation of nitro into nitrito [30–32]. All complexes show a new sharp band at ~825 cm^{-1} assigned as δ(ONO) nitrito, evidence for coordination of metal to oxygen of nitrito. This was supported by the appearance of ν(Ru–O) observed near 550 cm^{-1} [33]. In all the complexes one or two bands observed in the range 1096–1128 cm^{-1} were assigned for ν(SO). This band, which appears 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 ruthenium [34, 35]. In all the complexes the band near 400 cm^{-1} was assigned for Ru–S bond. A sharp band at 330 cm^{-1} was assigned for Ru–Cl stretching modes. In **3** and **7**, a broad band at ~730 cm^{-1}, along with a sharp band at 1054 cm^{-1} (dmso analogue) and 1028 cm^{-1} (tmso analogue), indicates the presence of hydrogen bonded dmso/tmso.

In ^{1}H-NMR spectra all the above complexes, multiplets for the seven aromatic protons, were observed between δ 8.37–6.79 ppm and in $^{13}C\{^1H\}$NMR spectra signals for 12 aromatic carbons were observed between δ 161–127 ppm [28].

In ^{1}H–NMR spectra of **1** four signals with intensity 1: 2: 1: 1 indicate four different types of protons. Signals at δ 3.62 ppm for six protons were assigned for methyl protons of dmso trans to oxygen of nitrito, the signals at δ 3.43 ppm and δ 3.29 ppm, for 12 and six protons, respectively, were assigned for the methyl protons of dmso trans to Cl which are diasterotropic to each other and the signal centered at δ 3.03 ppm, for six protons was assigned to methyl protons of dmso trans to cyclic nitrogen of *5-nitro-o*-phenanthroline [20, 36–38]. The $^{13}C\{^1H\}$-NMR spectra of **1** exhibit four signals for the methyl carbons of dmso. The signal at δ 45.9 ppm was assigned for methyl carbon of dmso trans to oxygen of nitrito group and signals at δ 44.8 and δ 44.2 ppm for diastereotropic methyl of dmso trans to Cl. The signal for methyl carbon of dmso trans to cyclic nitrogen of *o*-phenanthroline was observed at δ 42.6 ppm.

In ^{1}H–NMR spectra of **5**, five signals are observed, a multiplet at δ 4.18 ppm, assigned for four protons of S–CH_2 trans to oxygen of nitrito unit, multiplets at δ 4.03 ppm for four protons and δ 3.98 ppm for eight protons was assigned for S–CH_2 protons of tmso trans to Cl, a multiplet at δ 3.44 ppm for four protons of S–CH_2 trans to cyclic nitrogen of *o*-phenanthroline, and a multiplet at δ 2.32 ppm for 20 protons of all S–C–CH_2 groups. These five signals were in ratio 1: 1: 2: 1: 5 [39, 40]. Similar conclusion can be drawn from $^{13}C\{^1H\}$-NMR spectra. The signals are assigned as δ 57.9 ppm for (S–C) carbon of tmso trans to nitrito, δ 54.7 and δ 54.1 ppm for the (S–C) carbon of tmso trans to Cl and δ 53.1 ppm for the (S–C) carbon trans to nitrogen of



Complex **1** Complex **5**

Figure 1. Structures of **1** and **5**.

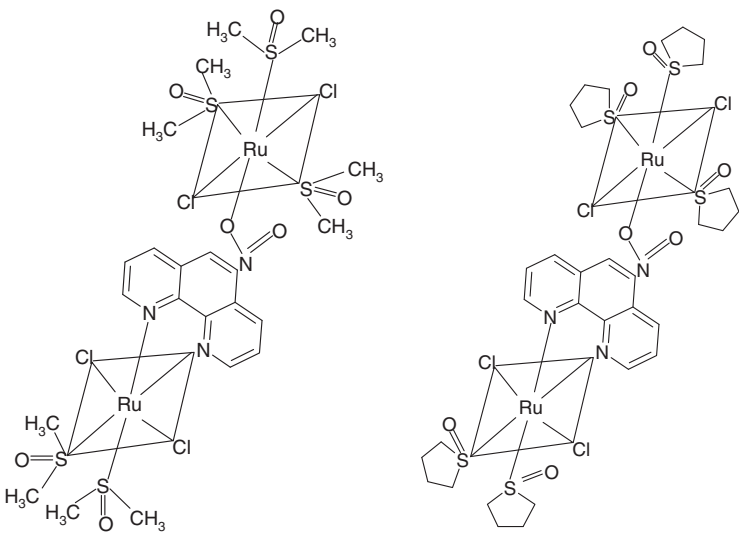
o-phenanthroline. Signals at δ 27.4, δ 26.8, δ 26.3, and δ 24.1 ppm were assigned for the (S–C–C) carbon of tmso. Thus on the basis of CHN analyses, UV-Vis, FT-IR, FAB-Mass, ^{1}H-NMR, and ^{13}C{^{1}H}-NMR spectra, probable structures of **1** and **5** are suggested in figure 1.

^{1}H-NMR spectra of **2** show three signals with intensity ratio 1: 2: 2, indicating three types of environment for CH_3 of dmso. The signal at δ 3.27 ppm (6H) was assigned for dmso trans to oxygen of nitrito, δ 3.08 ppm for dmso trans to *o*-phenanthroline and δ 3.05 ppm (12H) for dmso trans to each other.

In the ^{1}H–^{1}H COSY spectrum of **2** (Supplementary material), cross peaks were observed in the aromatic region due to the proton–proton coupling between connected carbons [27]. The signal at δ 6.89 ppm for H_3 is connected by cross peaks to the two separate signals at δ 8.28 ppm for H_2 and at δ 7.80 ppm for H_4, and the signal at δ 6.97 ppm for H_8 is connected to signals at δ 8.37 ppm for H_9 and δ 7.83 ppm for H_7 by cross peaks. No cross peaks were observed in the sulfoxide region showing no connectivity between the methyl carbons of dmso. Similar conclusions were derived from ^{13}C{^{1}H}-NMR spectra with three signals for (S–C) of dmso at δ 44.7, δ 42.9, and δ 42.1 ppm [20, 36–38].

Complex **6** exhibits four sets of multiplets at δ 4.01, δ 3.53, δ 3.42, and δ 3.35 ppm with δ 4.01, δ 3.53, and δ 3.42 ppm assigned to (S–CH_2) and δ 3.35 ppm for (S–C–CH_2) of tmso. Thus, one tmso is trans to nitrito of *o*-phenanthroline, two tmso are trans to cyclic nitrogens and the other two tmso are trans to each other. This is supported by ^{13}C{^{1}H}-NMR, where signals at δ 54.1, δ 53.9, and δ 53.3 ppm were assigned for (S–C) and δ 26.1, δ 23.9, and δ 23.3 ppm for (S–C–C) of tmso. Thus, on the basis of CHN analyses FT-IR, UV-Vis, FAB-Mass, ^{1}H-NMR, and ^{13}C{^{1}H}-NMR spectra structures of **2** and **6** are suggested [39–41] (figure 2).

NMR spectra of **3**, **4**, and **7** were too broad due to paramagnetic ion, but on the basis of UV-Vis spectra and FT-IR spectra it was evident that one Cl^- is replaced on one



Complex **2** Complex **6**

Figure 2. Structure of **2** and **6**.

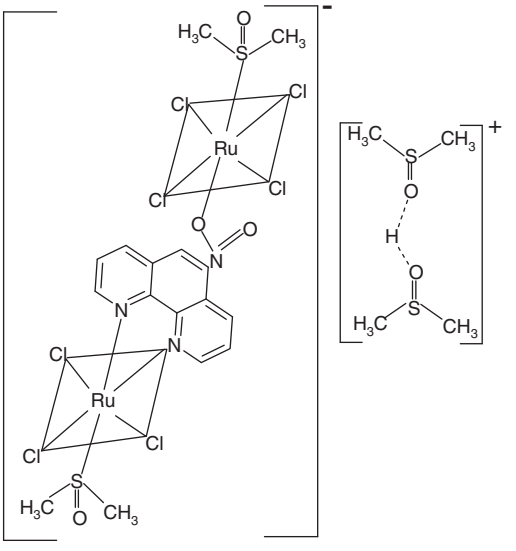
ruthenium along with a sulfoxide [21, 42]. Chloride was verified by silver nitrate test. Binding of ligand with Ru(III) was concluded on the basis of CHN analyses, UV-Vis, FT-IR, and FAB-Mass spectra with plausible structures of **3**, **4**, and **7** (figure 3).

6. Antibacterial screening

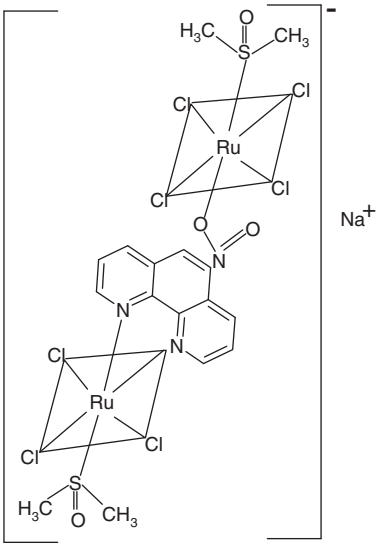
Complexes **1**–**7**, their precursors **1a**–**7a** and ligand **A** were screened for antibacterial properties against gram negative bacteria *Escherichia coli*, MTCC 1304 at different concentrations. Muller Hinton agar plates (MHA) were prepared and 50-μL suspension of *E. coli* containing approximately 10^5 CFU (Colony Forming Unit) was applied to the plate by the spread plate technique [43]. Wells are made on the plates and filled with 50 μL of sample solution of 0.02, 0.03, and 0.04% concentrations. The 0.02% solution of Chloramphenicol was used for comparison. These plates were incubated at $37 \pm 1^{\circ}$C for 24–48 h in incubator shakers. The results in the form of zone of inhibition were measured in mm. All precursors and their metal complexes show more activity than ligand [39, 44]. Complexes **3**, **4**, and **7** were found much potent in comparison to other complexes. The detailed result of antibacterial screening for 0.02% concentration is given in table 1 and photograph (Supplementary material, Figure S2).

7. Catalytic activity

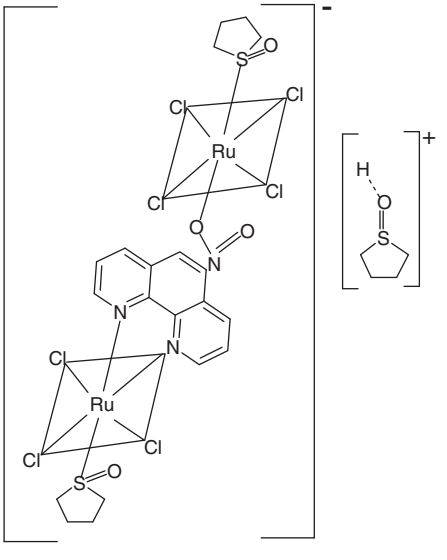
Ruthenium complexes have good catalytic properties in reactions such as decomposition of hydrogen peroxide [45]. Seven complexes were tested for catalytic hydrolysis of



Complex **3**



Complex **4**



Complex **7**

Figure 3. Structure of **3**, **4** and **7**.

benzonitrile in 25 mL of hydrogen peroxide. Reaction mixture was stirred for 5 min turning milky white. To this mixture 0.5 mL of 10% sodium hydroxide solution was added and stirred for 5 min. The reaction mixture was refluxed until the oily suspension of benzonitrile completely disappeared, and then allowed to cool. After cooling,

Table 1. Antibacterial screening against *E. coli*.

Complex/Precursor	Diameter of inhibition zone (in mm) ±SEM*
5-nitro-o-phenanthroline, Ligand	7.0 ± 0.8
[*cis,fac*-$RuCl_2(dmso)_3$(μ-*nphen*)*cis,cis*-$RuCl_2(dmso)_2$]	14.0 ± 0.5
[*cis,fac*-$RuCl_2$(S-dmso)$_3$(O-dmso)]	7.0 ± 0.8
[*trans,mer*-$RuCl_2(dmso)_3$(μ-*nphen*)*trans,cis*-$RuCl_2(dmso)_2$]	17 ± 1
[*trans*-$RuCl_2(dmso)_4$]	7.0 ± 0.9
$[(dmso)_2H]^+$[*trans*-$RuCl_4$(dmso)((μ-*nphen*)*mer*-$RuCl_3$(dmso)]$^-$	27 ± 2
$[(dmso)_2H]^+$[*trans*-$RuCl_4(dmso)\}_2]^-$	19 ± 2
$[Na]^+$[*trans*-$RuCl_4$(dmso)(μ-*nphen*)*mer*-$RuCl_3$(dmso)]$^-$	21 ± 2
$(Na)^+$[*trans*-$RuCl_4(dmso)_2]^-$	12 ± 2
[*cis,fac*-$RuCl_2(tmso)_3$(μ-*nphen*)*cis,cis*-$RuCl_2(tmso)_2$]	15 ± 1
[*cis*-$RuCl_2(tmso)_4$]	7.0 ± 0.5
[*trans,mer*-$RuCl_2(tmso)_3$(μ-*nphen*)*trans,cis*-$RuCl_2(tmso)_2$]	18 ± 1
[*trans*-$RuCl_2(tmso)_4$]	6.0 ± 0.8
$[(tmso)H]^+$[*trans*-$RuCl_4$(tmso)(μ-*nphen*)*mer*-$RuCl_3$(tmso)]$^-$	30 ± 2
$[(tmso)H]^+$ [*trans*-$RuCl_4(tmso)_2]^-$	9 ± 1
Chloramphenicol	40 ± 1

*Mean value of inhibition zone ± Standard error mean (SEM).

Table 2. Catalytic activity of the complexes.

Complex	Amount (μmole)	Weight of product (in gm) ±SEM[a]	Yield of product (%)	Turnover[b]
Control reaction	–	1.064 ± 0.006	59.8	–
1	18.8	1.26 ± 0.02	70.9	554.2
2	18.8	1.18 ± 0.06	66.6	520.2
3	14.4	1.2 ± 0.1	65.4	667.6
4	17.3	1.28 ± 0.03	72.1	612.8
5	14.5	1.26 ± 0.04	71.0	719.7
6	14.5	1.19 ± 0.05	67.1	680.2
7	18.0	1.28 ± 0.08	72.2	589.1

[a]Standard error mean (SEM).
[b]Moles of product per moles of catalysts.

white shiny crystals of benzamide were collected by filtration, washed with water and dried. A small amount of benzamide was isolated from the mother liquor after vacuum evaporation.

When 14.4–18.8 μM of complexes were added to the above reaction mixture, reaction time for completion was less than the control reaction and the yield of benzamide increased. The results are summarized in table 2.

8. Conclusion

Seven dinuclear ruthenium (II)/(III) complexes have been synthesized. In **1**, **2**, **5**, and **6** two sulfoxides were replaced on one ruthenium and one sulfoxide was replaced on the other ruthenium. In **3**, **4**, and **7**, one Cl was replaced along with a sulfoxide on

one ruthenium sulfoxide unit. These complexes have catalytic and biological activity. Their characterization, chemical reactivity, and inherent activity give a new look to ruthenium-based pharmaceuticals.

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References

[1] A. Bergamo, G. Stocco, C. Casarsa, H. Cocchietto, E. Alessio, B. Serli, S. Zorzet, G. Sava. *Inter. J. Onco*., **24**, 373 (2004).
[2] A.H. Velders, A. Bergamo, E. Alessio, E. Zangrando, J.G. Haasnoot, C. Casarsa, M. Cocchietto, S. Zorzet, G. Sava. *J. Med. Chem*., **47**, 1110 (2004).
[3] B. Serli, E. Zangrando, T. Gianferrara, L. Yellowlees, E. Alessio. *Coord. Chem. Rev*., **245**, 73 (2003).
[4] E. Alessio, G. Mestroni, G. Nardin, W.M. Attia, M. Calligaris, G. Sava, S. Zorzet. *Inorg. Chem*., **27**, 4099 (1988).
[5] E. Alessio, G. Balducci, M. Calligaris, G. Costa, W.M. Attia, G. Mestroni. *Inorg. Chem*., **30**, 609 (1991).
[6] G. Sava, K. Cleric, I. Capozzi, M. Cocchieto, R. Gagliardi, E. Alessio, G. Mestroni, A. Perbellini. *Anti Cancer Drugs*, **10**, 129 (1999).
[7] G. Sava, E. Alessio, E. Bergamo, G. Mestroni. *Top. Biol. Inorg. Chem*., **1**, 143 (1999).
[8] M. Henn, E. Alessio, G. Mestroni, M. Calligaris, W.M. Attia. *Inorg. Chim. Acta*, **187**, 39 (1991).
[9] E. Alessio, M. Calligaris, M. Iwamoto, L.G. Marzilli. *Inorg. Chem*., **35**, 2538 (1996).
[10] M.M. Taquikhan, N.H. Khan, R.I. Kureshy, K. Venkatasubramanian. *Polyhedron*, **11**, 431 (1992).
[11] M. Iwamoto, E. Alessio, L.G. Marzilli. *Inorg. Chem*., **35**, 2384 (1996).
[12] E. Alessio, E. Iengo, E. Zangrando, S. Geremia, P.A. Marzilli, M. Calligaris. *Eur. J. Inorg. Chem*., 2207 (2000).
[13] E. Alessio. *Chem. Rev*., **104**, 4203 (2004).
[14] J.A. Wright, C. Brodie, E.C. Glazer, N.W. Luedtke, L.E. Schwab, Y. Tor. *Chem. Commun*., 1018 (2004).
[15] O.V. Gijte, A.A. Kirsch-De-Mesmaeker. *J. Chem. Soc., Dalton Trans*., 951 (1999).
[16] A. Brodkorb, A.A. Kirsch-De-Mesmaeker, T. Rutherford, F.R. Keene. *Eur. J. Inorg. Chem*., 2151 (2001).
[17] L. Mishra, A.K. Yadav. *Ind. J. Chem*., **42A**, 1797 (2003).
[18] P. Paul, B. Tyagi, P. Natarajan. *Ind. J. Chem*., **42A**, 2283 (2003).
[19] B.E. Halcrow, W.O. Kermack. *J. Chem. Soc*., 155 (1946).
[20] I.P. Evans, A. Spencer, G. Wilkinson. *J. Chem. Soc., Dalton Trans*., 204 (1973).
[21] E. Alessio, B. Milani, G. Mestroni, M. Calligaris, P. Faleschini, W.M. Attia. *Inorg. Chim. Acta*, **177**, 255 (1990).
[22] T. Bora, M.M. Singh. *Transition Met. Chem*., **3**, 27 (1978).
[23] U.C. Sarma, R.K. Poddar. *Polyhedron*, **7**(18), 1737 (1988).
[24] A.B.P. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, Elsevier, Amsterdam, The Netherlands (1984).
[25] S. Dutta, P.K. Bhattacharya. *Ind. J. Chem*., **42A**, 262 (2003).

[26] B.R. James, R.H. Morris. *Can. J. Chem.*, **58**, 399 (1980).
[27] R.M. Silverstein, G.C. Bassler, T.C. Morrill. *Spectrometric Identification of Organic Compounds*, p. 131,272, John Wiley and Sons, Inc, New York (1991).
[28] J. Canivet, L.K. Brelot, G.S. Fink. *J. Organomet. Chem.*, **690**, 3202 (2005).
[29] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*, 5th Edn, p. 50, John Wiley and Sons, Inc, New York (1922).
[30] I.N. Kukuszkin. *Koord. Chim.*, **4**, 1170 (1972).
[31] D.L. Goodgame, M.A. Hitchman. *Inorg. Chem.*, **6**, 813 (1987).
[32] W. Ferenc, B. Bocian, D. Mazur. *Croat. Chem. Acta*, **72**, 779 (1999).
[33] B. Serli, E. Zangrando, E. Lengo, G. Mestroni, L. Yellowlees, E. Alessio. *Inorg. Chem.*, **41**, 4033 (2002).
[34] W.L. Reynolds. *Prog. Inorg. Chem.*, **12**, 1 (1970).
[35] J.A. Davis. *Adv. Inorg. Chem. Radiochem.*, **24**, 115 (1981).
[36] T. Bora, M.M. Singh. *J. Inorg. Nucl. Chem.*, **38**, 1815 (1976).
[37] J.D. Fortheringham, G.A. Heath, A.J. Lindsay, T.A. Stephensen. *J. Chem. Res.*, **82**, 801 (1986).
[38] J.D. Oliver, D.P. Riley. *Inorg. Chem.*, **23**, 156 (1984).
[39] P.K.L. Chan, B.R. James, D.C. Frost, P.K.H. Chan, H.L. Hu, K.A. Skov. *Can. J. Chem.*, **67**, 508 (1989).
[40] F.D. Rochon, P.C. Kong, L. Girard. *Can. J. Chem.*, **64**, 1897 (1986).
[41] J.H. Price, A.N. Williamson, R.F. Schramm, B.B. Wayland. *Inorg. Chem.*, **11**, 1280 (1972).
[42] R.S. Srivastava, F.R. Fronczek. *Inorg. Chim. Acta*, **358**, 854 (2005).
[43] M.J. Pelczar, E.C.S. Chan, N.R. Krieg. *Text Book of Microbiology*, 5th Edn, p. 138, McGraw-Hill Publishing Company Ltd., New Delhi, India (2001).
[44] R. Malhotra, S. Kumar, K.S. Dhinds. *Ind. J. Chem.*, **32A**, 457 (1993).
[45] S.I. Murahashi, H. Takaya, T. Naota. *Pure Appl. Chem.*, **74**, 19 (2002).