

Mononuclear and binuclear ruthenium(III) complexes of macrocyclic compartmental ligands : synthetic, spectral speciation, electrochemical behaviour and antimicrobial studies

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Abstract : The macrocyclic compartmental Schiff base ruthenium(III) complexes have been synthesized. A variety of complexes have been obtained by different procedures and also depending on the choice of lateral diamine fragments with ruthenium ions. The compounds were characterized by elemental analyses, conductometric and magnetochemical behaviour, as well as by IR, ESR, TG, electrochemical and electronic spectra. The antimicrobial activities of the ligands and the complexes have also been tested.

Keywords : Schiff base, ruthenium(III), compartmental ligands.

Recent years have witnessed discernible growth in interest in cyclic and macrocyclic compartmental complexes of transition metals because of their use as diagnostic agents in magnetic resonance imaging¹. A variety of complexes of macrocyclic ligands obtained in 2+1 or 2+2 condensation of 2,6-diformyl-4-methylphenol with diamines in the presence of metal ions can be obtained by quite different procedures, depending on the choice of lateral diamine fragments and metal ions². Ruthenium(III) complexes, by virtue of their wide range receives ample attention due to the fascinating properties of reversible and accessible oxidation states. Binuclear ruthenium(III) complexes are of contemporary relevance due to their magnetic, catalytic and electron transfer properties and as models of bioinorganic chemistry³. *N,N'*-ethylenebis(3-formyl-5-methylsalicylaldehyde), *N,N'*-propylenebis(3-formyl-5-methylsalicylaldehyde) and *N,N'*-*o*-phenylenebis(3-formyl-5-methylsalicylaldehyde) is an extensively studied salen type ligands. Surprisingly, to the best of our knowledge, its ruthenium(III) complexes in 2 : 1 : 1 ratio and 2 : 2 : 1 template condensation with 2,6-diformyl-4-methylphenol with various diamines in the presence of ruthenium(III) has not yet been reported. Same ligands may be used to synthesize binuclear complexes with a second metal ion in close proximity to the ruthenium(III) center. Further understanding of metal-metal interactions is very important because bimetallic cores exist at the

active sites of many metalloenzymes and play essential roles in biological systems by the interplay of a pair of metal ion⁴.

Compartmental ligands are candidates for the provision of distinct coordination environment⁵. Many of these sub group binucleating ligands have been derived from 4- (or) 3,4-disubstituted phenols. Ligands of this type readily form binuclear transition metal complexes that can coordinate with either one or two exogenous bridging units⁶. These ligands strongly favour the formation of bimetallic species because of the enforced ideal distance between the donor sites and the presence of the bridging phenolato groups.

Experimental

Materials : Commercial RuCl₃·3H₂O purchased from Loba Chemie, Bombay was converted into RuCl₃·3H₂O by repeated evaporation to dryness with conc. HCl. Solvents were purified and dried according to the literature procedures⁷. Published method in modified way is used to synthesize 2,6-diformyl-4-methylphenol. Ethylenediamine, 1,3-propylenediamine and *o*-phenylenediamine were obtained from Aldrich. *N,N'*-ethylenebis(3-formyl-5-methylsalicylaldehyde) (H₂L₁), *N,N'*-propylenebis(3-formyl-5-methylsalicylaldehyde) (H₂L₂) and *N,N'*-*o*-phenylenebis(3-formyl-5-methylsalicylaldehyde) (H₂L₃) were prepared according to the published procedure⁸.

Physical measurements : The elemental analyses were obtained from the Microanalytical Laboratory of CDRI, Lucknow, India. Metals and chlorides were determined volumetrically and gravimetrically. Electronic spectra were recorded using dimethyl formamide solutions in 1 cm cells with a Perkin-Elmer Lambda 15 UV/Vis spectrophotometer. IR spectra were scanned in KBr pellet on a Perkin-Elmer PC-16F FTIR spectrophotometer in the 4000–350 cm^{-1} regions. Magnetic susceptibility measurement were carried out at room temperature by Gouy's balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as a calibrant. The conductivity measurement were made using Systronic conductivity meter with a dip type cell, using approximately 10^{-3} M solution of the complexes in DMF. Molecular FAB mass spectra were obtained on a JEOL SX 102/DA-6000 mass spectrometer using *m*-nitrobenzyl alcohol (NBA) as a matrix. The ESR spectra of the complexes were recorded on a Varian E-4X-band spectrometer. The thermogravimetric data were obtained in air at $10^\circ\text{C min}^{-1}$ in the 25–750 $^\circ\text{C}$ range using a Shimadzu TGA-50 analyzer. Electrochemical results were collected with a BAS CV-27 electrochemical analyzer and a BAS Model X-Y recorder at 298 K.

Synthesis of the complexes :

(i) $[\text{Ru}(\text{H}_2\text{L}_1)(\text{Cl}_2)]\text{Cl} \cdot 2\text{H}_2\text{O}$: A typical procedure is followed. An ethanolic solution of ruthenium(III) chloride trihydrate (0.216 g; 1.0 mmol) was added to a solution of H_2L_1 (0.352 g; 1.0 mmol) in warm ethanol. It soon gave dark brown precipitate, which was refluxed with stirring for next 4 h. The resulting mixture was filtered, washed with ethanol ($2 \times 5 \text{ cm}^3$) and dried *in vacuo*. The yield was 0.370 g (60%) (Found : C, 42.6; H, 3.6; N, 4.8; Cl, 18.3; Ru, 18.6. Calcd. for $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_4\text{Cl}_3\text{Ru}$: C, 42.9; H, 3.6; N, 5.0; Cl, 18.7; Ru, 18.2%); m.p. 255°C . Mol. W., 572, *m/z*, 538. Selected IR data [v/cm^{-1}] using KBr discs : 3190 (N-H), 1630, 1650 (C=N), 1550 (C-O), 1540 (skeletal vibration). Molar conductance [$\Lambda_{\text{M}}/\text{S cm}^2 \text{ mol}^{-1}$] in EtOH, 108. UV-vis data [$\lambda/(\epsilon/\text{M}^{-1} \text{ cm}^{-1})$] in EtOH, 13500, 17450, 23000.

(ii) $[\text{Ru}(\text{H}_2\text{L}_2)(\text{Cl}_2)]\text{Cl} \cdot 2\text{H}_2\text{O}$: Complex is prepared in similar fashion in 0.430 g (68%) yield (Found : C, 43.6; H, 3.6; N, 4.5; Cl, 18.0; Ru, 17.6. Calcd. for $\text{C}_{21}\text{H}_{22}\text{N}_2\text{O}_4\text{Cl}_3\text{Ru}$: C, 43.9; H, 3.8; N, 4.8; Cl, 18.3; Ru, 17.7%); m.p. 230°C . Mol. W., 606, *m/z*, 571. Selected IR data [v/cm^{-1}] using KBr discs : 3100 (N-H), 1600, 1640 (C=N), 1565 (C-O), 1542 (skeletal vibration). Molar conductance [$\Lambda_{\text{M}}/\text{S cm}^2 \text{ mol}^{-1}$] in EtOH,

118. UV-vis data [$\lambda/(\epsilon/\text{M}^{-1} \text{ cm}^{-1})$] in EtOH, 13800, 17900, 23200.

(iii) $[\text{Ru}(\text{H}_2\text{L}_3)(\text{Cl}_2)]\text{Cl} \cdot 2\text{H}_2\text{O}$: Complex is prepared in similar fashion in 0.490 g (74%) yield (Found : C, 47.1; H, 3.6; N, 4.5; Cl, 17.0; Ru, 16.3. Calcd. for $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_4\text{Cl}_3\text{Ru}$: C, 47.4; H, 3.3; N, 4.6; Cl, 17.2; Ru, 16.7%); m.p. 242°C . Mol. W., 558, *m/z*, 523. Selected IR data [v/cm^{-1}] using KBr discs : 3072 (N-H), 1630, 1655 (C=N), 1560 (C-O), 1546 (skeletal vibration). Molar conductance [$\Lambda_{\text{M}}/\text{S cm}^2 \text{ mol}^{-1}$] in EtOH, 125. UV-vis data [$\lambda/(\epsilon/\text{M}^{-1} \text{ cm}^{-1})$] in EtOH, 14000, 18100, 22800.

(iv) $[\text{Ru}_2(\text{L}'_1)(\text{Cl}_3)]\text{Cl} \cdot \text{H}_2\text{O}$: To a solution of $[\text{Ru}(\text{H}_2\text{L}_1)(\text{Cl}_2)]\text{Cl} \cdot 2\text{H}_2\text{O}$ (0.921 g; 1.5 mmol) in ethanol (20 cm^3), aniline (0.4 cm^3 ; 4.5 mmol) in ethanol was added dropwise with constant stirring at room temperature. After an hour solid RuCl_3 (0.388 g; 1.8 mmol) was added to it. The mixture was then refluxed for next 8 h. Solvent was removed partially on a rotatory evaporator and the dark red coloured product was isolated by filtration, washed with ethanol and dried in vacuum desiccator. The yield was 0.990 g (58%) (Found : C, 45.2; H, 3.0; N, 6.2; Cl, 16.1; Ru, 24.0. Calcd. for $\text{C}_{32}\text{H}_{28}\text{N}_4\text{O}_2\text{Cl}_4\text{Ru}_2$: C, 45.5; H, 3.3; N, 6.6; Cl, 16.5; Ru, 24.1%); m.p. $>360^\circ\text{C}$. Mol. W., 843, *m/z*, 808. Selected IR data [v/cm^{-1}] using KBr discs : 1629 (C=N), 1550 (skeletal vibration). Molar conductance [$\Lambda_{\text{M}}/\text{S cm}^2 \text{ mol}^{-1}$] in EtOH, 98. UV-vis data [$\lambda/(\epsilon/\text{M}^{-1} \text{ cm}^{-1})$] in EtOH, 12560, 17000, 24000.

(v) $[\text{Ru}_2(\text{L}'_2)(\text{Cl}_3)]\text{Cl} \cdot \text{H}_2\text{O}$: This complex (dark blue in colour) is prepared by similar procedures to those discussed above (iv) in 1.180 g (68%) yield (Found : C, 45.8; H, 3.2; N, 6.2; Cl, 16.1; Ru, 23.3. Calcd. for $\text{C}_{33}\text{H}_{30}\text{N}_4\text{O}_2\text{Cl}_4\text{Ru}_2$: C, 46.1; H, 3.5; N, 6.5; Cl, 16.3; Ru, 23.7%); m.p. $>360^\circ\text{C}$. Mol. W., 857, *m/z*, 822. Selected IR data [v/cm^{-1}] using KBr discs : 1635 (C=N), 1552 (skeletal vibration). Molar conductance [$\Lambda_{\text{M}}/\text{S cm}^2 \text{ mol}^{-1}$] in EtOH, 112. UV-vis data [$\lambda/(\epsilon/\text{M}^{-1} \text{ cm}^{-1})$] in EtOH, 12700, 17160, 23900.

(vi) $[\text{Ru}_2(\text{L}'_3)(\text{Cl}_3)]\text{Cl} \cdot \text{H}_2\text{O}$: This complex (dark blue in colour) is prepared by similar procedures to those discussed above (iv) in 1.380 g (70%) yield (Found : C, 48.1; H, 3.0; N, 6.2; Cl, 15.3; Ru, 22.5. Calcd. for $\text{C}_{36}\text{H}_{28}\text{N}_4\text{O}_2\text{Cl}_4\text{Ru}_2$: C, 48.4; H, 3.1; N, 6.2; Cl, 15.6; Ru, 22.8%); m.p. $>360^\circ\text{C}$. Mol. W., 891, *m/z*, 856. Selected IR data [v/cm^{-1}] using KBr discs : 1630 (C=N), 1556 (skeletal vibration). Molar conductance : [$\Lambda_{\text{M}}/\text{S cm}^2 \text{ mol}^{-1}$] in EtOH, 122. UV-vis data [$\lambda/(\epsilon/\text{M}^{-1} \text{ cm}^{-1})$] in

EtOH, 12650, 17150, 24100.

(vii) $[Ru(L'_1)]Cl.NH_2(CH_2)_2NH_2.2EtOH$: To a boiling solution of $RuCl_3.3H_2O$ (0.522 g; 2.0 mmol) and 2,6-diformyl-4-methylphenol (0.656 g; 4.0 mmol) in ethanol (35 cm³), an ethanolic solution of the ethylenediamine (0.267 g; 4.0 mmol) was added slowly with constant stirring and the mixture was boiled under reflux for 12 h. A greenish black precipitate was formed which was filtered, washed with ethanol (3 × 5 cm³) and then dried in air. The yield was 0.890 g (62%) (Found : C, 51.4; H, 4.0; N, 10.7; Cl, 6.6; Ru, 19.6. Calcd. for $C_{22}H_{22}N_4O_2ClRu$: C, 51.6; H, 4.3; N, 10.9; Cl, 6.8; Ru, 19.9%); m.p. >360 °C. Mol. W., 511, m/z , 476. Selected IR data [ν/cm^{-1}] using KBr discs : 3160 (N-H), 1650 (C-O), 1580 (C=N), 1550 (C...O). Molar conductance [$\Lambda_M/S\ cm^2\ mol^{-1}$] in EtOH, 131. UV-vis data [$\lambda/(\epsilon/M^{-1}\ cm^{-1})$] in EtOH, 14200, 17600, 22300.

(viii) $[Ru(L'_2)]Cl.NH_2(CH_2)_3NH_2.2EtOH$: This complex (green in colour) is prepared by similar procedures to those discussed above (vii) in 1.020 g (68%) yield (Found : C, 53.1; H, 4.4; N, 10.7; Cl, 6.6; Ru, 18.6. Calcd. for $C_{24}H_{26}N_4O_2ClRu$: C, 53.4; H, 4.8; N, 10.3; Cl, 6.4; Ru, 18.9%); m.p. >360 °C. Mol. W., 539, m/z , 504. Selected IR data [ν/cm^{-1}] using KBr discs : 3170 (N-H), 1635 (C-O), 1590 (C=N), 1545 (C...O). Molar conductance [$\Lambda_M/S\ cm^2\ mol^{-1}$] in EtOH, 105. UV-vis data [$\lambda/(\epsilon/M^{-1}\ cm^{-1})$] in EtOH, 14150, 17700, 22000.

(ix) $[Ru(L'_3)]Cl.NH_2(C_6H_4)NH_2.2EtOH$: This complex (dark brown in colour) is prepared by similar procedures to those discussed above (vii) in 0.930 g (58%) yield (Found : C, 53.1; H, 4.4; N, 10.7; Cl, 6.6; Ru, 18.6. Calcd. for $C_{30}H_{22}N_4O_2ClRu$: C, 59.3; H, 3.6; N, 9.2; Cl, 5.7; Ru, 16.7%); m.p. >360 °C. Mol. W., 607, m/z , 572. Selected IR data [ν/cm^{-1}] using KBr discs : 3120 (N-H), 1645 (C-O), 1586 (C=N), 1530 (C...O). Molar conductance [$\Lambda_M/S\ cm^2\ mol^{-1}$] in EtOH, 115. UV-vis data [$\lambda/(\epsilon/M^{-1}\ cm^{-1})$] in EtOH, 14100, 18000, 22900.

Qualitative antimicrobial assay : The *in vitro* biological screening⁹ effects of the investigated compounds were tested against six bacteria : *Escherichia coli* (E.c.), *Staphylococcus aureus* (S.a.), *Bacillus subtilis* (B.s.), *Salmonella typhi* (S.t.), *Pseudomonas aeruginosa* (P.a.), *Shigella flexneri* (S.f.) and two fungi : *Aspergillus niger* (A.n.) and *Fusarium oxysporium* (F.o.). Nutrient agar medium for both bacteria and fungi was poured into the sterilized Petri dishes and allowed to solidify. The plates were inoculated with a spore suspension of the test microorganisms, respectively. The test solution were pre-

pared in ethanol and soaked in filter paper discs (Whatmann no.1). The discs were placed on the already seeded plates [incubation period : 24 °C for bacteria (24 h); 26 °C for fungi (36 h)]. After 2 days, the inhibition zone, which appears around the discs in each plate, was measured. To avoid the activity of the solvent used in the test solutions, a solvent only treated plate was maintained. An untreated control plate was also maintained in order to calculate the percentage of inhibition.

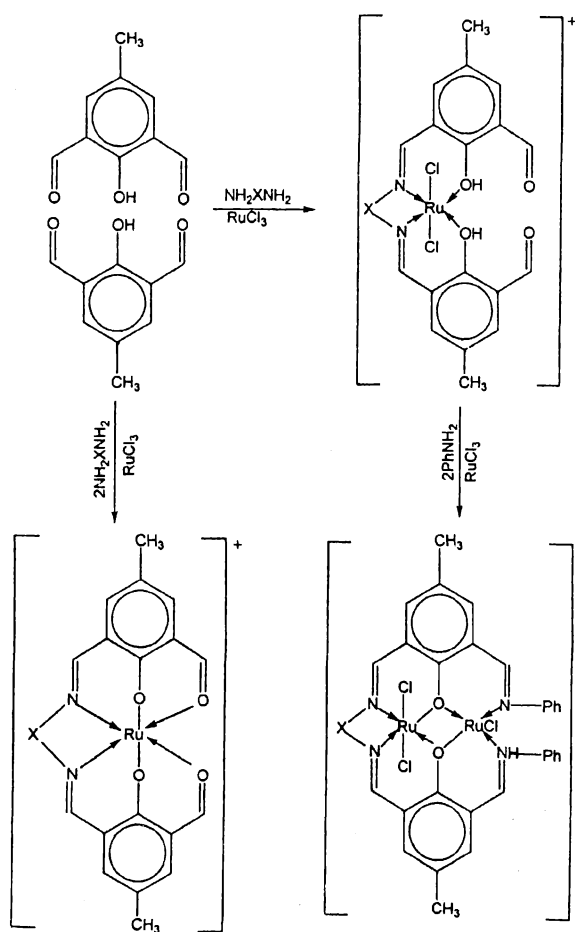
Results and discussion

Condensation of two molecules of 2,6-diformyl-4-methylphenol with one molecule of ethylenediamine, propylenediamine or *o*-phenylenediamine affords the monomeric Schiff bases, H_2L_1 , H_2L_2 or H_2L_3 in quantitative yield with no formation of polymer. Three types of nine complexes both monomeric and dimeric were prepared (Scheme 1). All the complexes are stable at room temperature and are very soluble in polar organic solvents, such as EtOH, $CHCl_3$, MeOH and quite less soluble in non-polar solvents, such as Et_2O and C_6H_6 . The ligands as well as complexes were obtained in decent yields (ca. 60–80%, respectively). The hot solutions of the ligands or ruthenium(III) chloride were used during complexation. Attempts to crystallize the complexes in different solvents failed.

Electronic spectra : The complexes formed very intensely coloured solutions and thus very low concentrations have been used. All the ruthenium(III) complexes are paramagnetic, indicating the presence of the metal ion in its +3 oxidation state. Both the monomeric and dimeric complexes showed three bands in the region 12500–14200, 17000–18100 and 22000–24100 cm^{-1} , which may be assigned to transitions, $^2T_{2g} \rightarrow ^4T_{1g}$, $^2T_{2g} \rightarrow ^4T_{2g}$ and $^2T_{2g} \rightarrow ^2A_{2g}$, $^4T_{1g}$ transitions with charge transfer bands, respectively. All of the mononuclear complexes have the nearest coordination sphere with O_h symmetry, where as the binuclear complexes shows three absorption bands generated by charge transfer, which is in good agreement with the data¹⁰ and also confirms that central ion configuration d^5 causes low spin state. All the observed band lie in the typical range of ligand to metal charge transfer transitions of (iv), (v) and (vi) ruthenium(III) complexes. The observed values of $10Dq$ are usually associated with considerable electron delocalization as an overall effect of covalent bonding. The calculated values of the B , C , β and $10Dq$ parameters (Table 1) confirm the proposed structure of the complexes (Scheme 1).

Table 1. Electronic spectral data of the ruthenium(III) complexes

Complexes	Localization of the absorption bands in cm^{-1}			ν_2/ν_1	$10Dq$	B	C	β
	${}^2T_{2g} \rightarrow {}^4T_{1g}$ (ν_1)	${}^2T_{2g} \rightarrow {}^4T_{2g}$ (ν_2)	${}^2T_{2g} \rightarrow {}^4A_{2g}, {}^4T_{1g}$ (ν_3)					
$[\text{Ru}(\text{H}_2\text{L}_1)(\text{Cl}_2)]\text{Cl} \cdot 2\text{H}_2\text{O}$ (i)	13500	17450	23000	1.29	26660.0	493.8	2672.9	0.79
$[\text{Ru}(\text{H}_2\text{L}_2)(\text{Cl}_2)]\text{Cl} \cdot 2\text{H}_2\text{O}$ (ii)	13800	17900	23200	1.29	26845.7	512.5	2620.8	0.82
$[\text{Ru}(\text{H}_2\text{L}_3)(\text{Cl}_2)]\text{Cl} \cdot 2\text{H}_2\text{O}$ (iii)	14000	18100	22800	1.29	26245.8	512.5	2420.8	0.82
$[\text{Ru}_2(\text{L}'_1)(\text{Cl}_3)]\text{Cl} \cdot \text{H}_2\text{O}$ (iv)	12560	17000	24000	1.35	28368.3	555.0	3258.3	0.88
$[\text{Ru}_2(\text{L}'_2)(\text{Cl}_3)]\text{Cl} \cdot \text{H}_2\text{O}$ (v)	12700	17160	23900	1.35	28190.8	557.5	3175.8	0.89
$[\text{Ru}_2(\text{L}'_3)(\text{Cl}_3)]\text{Cl} \cdot \text{H}_2\text{O}$ (vi)	12650	17150	24100	1.36	28479.0	562.5	3258.3	0.90
$[\text{Ru}(\text{L}'_1)]\text{Cl} \cdot \text{NH}_2(\text{CH}_2)_2\text{NH}_2 \cdot 2\text{EtOH}$ (vii)	14200	17600	22300	1.24	25425.0	425.0	2275.0	0.68
$[\text{Ru}(\text{L}'_2)]\text{Cl} \cdot \text{NH}_2(\text{CH}_2)_3\text{NH}_2 \cdot 2\text{EtOH}$ (viii)	14150	17700	22000	1.25	25060.4	443.8	2172.9	0.71
$[\text{Ru}(\text{L}'_3)]\text{Cl} \cdot \text{NH}_2(\text{C}_6\text{H}_4)\text{NH}_2 \cdot 2\text{EtOH}$ (ix)	14100	18000	22900	1.28	26320.8	487.5	2445.8	0.78


Scheme 1. $X = (\text{CH}_2)_2 : \text{H}_2\text{L}_1; (\text{CH}_2)_3 : \text{H}_2\text{L}_2; (\text{C}_6\text{H}_4) : \text{H}_2\text{L}_3$.

Magnetic susceptibility measurements : The magnetic susceptibility measurement of the ruthenium(III) complexes was observed at room temperature. The spin-only values

were calculated using the equations $\mu_{\text{Ru}} = 2[S_{\text{Ru}}(S_{\text{Ru}} + 1)]^{1/2}$ for complexes (i), (ii), (iii), (vii), (viii) and (ix) and it lie in the range 1.22–1.26 B.M. and are markedly equal to/or higher than spin-only value for one unpaired electron for low spin t_{2g}^5 ruthenium(III) in an octahedral environment. The magnetic moment of binuclear complexes (iv), (v) and (vi) were calculated by $\mu_{\text{Ru-Ru}} = (\mu_{\text{Ru}}^2 + \mu_{\text{Ru}}^2)^{1/2}$ and it lie in the range 1.72–1.75 B.M. range. These low values might be indicative of metal-metal interactions in the dimeric structures. The effective magnetic moment of complexes agreed well with that predicted for a low-spin d^5 configuration¹¹. Ruthenium(III) ion in the complexes are in good agreement with their corresponding spin-only value assuming no magnetic interaction between the metal ions. Therefore, these data indicate that both ruthenium(III) metals are in low-spin states.

ESR spectra : The solid state ESR spectra of X-band frequencies of the new ruthenium(III) complexes have been recorded at room temperature. The ESR spectrum is studied for the nature and extent of the subtle distortions of octahedral environment of low spin d^5 -ions. The nature and pattern of the spectra showed that binuclear complexes (iv), (v) and (vi) in the solid state gave broad signals in the low and high-field regions due to spin-exchange interactions between the two ruthenium(III) ions. It showed that they are similar to that of a monomer with one unpaired electron on the ruthenium(III) ion. However, complexes (i), (ii) and (iii) shows an isotropic spectrum with $g_{\text{iso}} = 2.13$, 2.17 and 2.18, respectively a characteristic of octahedral ruthenium(III) complexes¹². The spectra of the complexes (vii), (viii) and (ix) are

characteristic of a low-spin d^5 configurations. The g -tensors are anisotropic. The spectra exhibit two signals assigned to g_{\parallel} (2.32, 2.29 and 2.26), g_{\perp} (2.10), with g_{iso} (2.18, 2.16 and 2.15), respectively (Table 2) which are characteristic of an octahedral geometry with a d_{xz} ground

Table 2. ESR spectral data of the ruthenium(III) complexes

Complexes	g_x	g_y	g_z	$\langle g \rangle^*$
(i)	2.16	2.16	2.09	2.13
(ii)	2.19	2.19	2.13	2.17
(iii)	2.21	2.21	2.13	2.18
(iv)	2.02	2.05	2.12	2.06
(v)	2.07	2.08	2.13	2.09
(vi)	2.05	2.06	2.12	2.07
(vii)	2.10	2.10	2.32	2.18
(viii)	2.08	2.08	2.29	2.16
(ix)	2.11	2.11	2.26	2.15

$$\langle g \rangle^* = (1/3g_x^2 + 1/3g_y^2 + 1/3g_z^2)^{1/2}.$$

state¹³. The g values for the complexes with a $^2T_{2g}$ ground state ($g_{\parallel} > g_{\perp}$) may be expressed by the following equations^{12,14}:

$$g_{\parallel} = 2.002 - (8K_{\parallel}^2 \lambda^0 / \Delta E_{xy}) \quad (1)$$

$$g_{\perp} = 2.002 - (2K_{\perp}^2 \lambda^0 / \Delta E_{xz}) \quad (2)$$

where K_{\parallel} and K_{\perp} are the parallel and perpendicular components, respectively, of the orbital reduction factor (K). λ^0 is the spin orbit coupling constant. $\Delta E_{xy} = \Delta E_{x^2-y^2} = 12.345$ and 11.764 cm^{-1} and $\Delta E_{xz} = \Delta E_{x^2-y^2} = 20000$ and 20408 cm^{-1} are the electron transition energies, respectively. From the above relations, the orbital reduction factors (K_{\parallel} , K_{\perp} , K) that are a measure of covalence^{14,15} may be calculated. For an ionic environment, $K > 1$, and for a covalent environment, $K < 1$; the lower the value of K , the greater is the covalent character:

$$K_{\parallel}^2 = (g_{\parallel} - 2.002) \Delta E_{xy} / 8\lambda^0$$

$$K_{\perp}^2 = (g_{\perp} - 2.002) \Delta E_{xz} / 2\lambda^0$$

The K values of complexes i.e. less than 1 indicate mixed ionic-covalent bond character in these complexes. The nature and pattern of the ESR spectra showed that they are similar to that of a monomer with one unpaired electron on the ruthenium(III) ion. However these new complexes are dimers with one unpaired electron on each

ruthenium(III) ion leading to an S value of 1. The pairing of unpaired electrons is prevented by the longer distance between the two ruthenium(III) atoms provided by the bridging compartmental ligands. Hence, the ESR spectra of the new binuclear complexes follows to that of monomer with one unpaired electron¹⁶.

Infrared spectra: The important IR spectral bands of the free ligands were compared with those of the ruthenium(III) complexes to study the binding mode of the ligands to ruthenium ion in the complexes. The IR spectra of H_2L_1 , H_2L_2 and H_2L_3 show weak broad bands at $2610\text{--}2880 \text{ cm}^{-1}$. The bands can be ascribed to O-H stretching vibrations, which are known to shift significantly to lower frequencies as a result of OH---N intramolecular hydrogen bonding. The bands around $1670\text{--}1680$ and $1628\text{--}1635 \text{ cm}^{-1}$ can be assigned to the C=O and C=N stretching vibrations, respectively¹⁷. The bands observed in the region $3072\text{--}3190 \text{ cm}^{-1}$ in the complex are assigned to N-H stretching. The low value of $\nu(\text{N-H})$ is attributed to hydrogen bonding. The presence of C=N stretching vibrations in the spectra of the complex (i) around 1630 and 1650 cm^{-1} in (ii) around 1600 and 1640 cm^{-1} and in (iii) at 1638 and 1655 cm^{-1} suggests that only one arm of the formyl group of the phenolic unit is involved in coordination¹⁸. The bands at 1630 in (i), 1600 in (ii) and 1638 cm^{-1} in (iii) are at a frequency lower by approximately $11\text{--}20 \text{ cm}^{-1}$, than those in the free ligands. This can be ascribed to the withdrawn of electron density from the nitrogen atom owing to coordination. The band observed at $1550\text{--}1565 \text{ cm}^{-1}$ has been assigned due to the $\nu(\text{C}\cdots\text{O})$ vibrations of the phenol as a consequence of the delocalisation of double bond in the chelate rings that has increased the bond order of the phenolic C-O¹⁹. The band observed at $1650\text{--}1660 \text{ cm}^{-1}$ assigned to C=O in (i), (ii) and (iii) is absent in the spectra of all the binuclear complexes (iv), (v) and (vi) suggesting the complete condensation of the formyl groups of complexes of H_2L_1 (i), H_2L_2 (ii) and H_2L_3 (iii) with aniline. Complexes (vii), (viii) and (ix) display a $\nu(\text{C=O})$ band at $1635\text{--}1650 \text{ cm}^{-1}$ and a $\nu(\text{C=N})$ vibration at $1580\text{--}1590 \text{ cm}^{-1}$. The bands at 3120 and 3170 cm^{-1} are assigned to $\nu(\text{NH})$ vibrations. The low value of $\nu(\text{NH})$ is attributed to the fact that the NH_2 group is coordinated to the metal.

Table 3. Antimicrobial activity data of ligands and the ruthenium(III) complexes

Table 3. Antimicrobial activity data of ligands and the ruthenium(III) complexes																			
Compd.	Antibacterial activity, diameter of inhibition zone (mm)												Antifungal activity % inhibition zone ($\mu\text{g ml}^{-1}$)						
	<i>E.c.</i>		<i>S.a.</i>		<i>B.s.</i>		<i>S.t.</i>		<i>P.a.</i>		<i>S.f.</i>		<i>A.n.</i>		<i>F.o.</i>				
	100 ppm	500 ppm	100 ppm	500 ppm	100 ppm	500 ppm	100 ppm	500 ppm	100 ppm	500 ppm	100 ppm	500 ppm	50 ppm	100 ppm	50 ppm	100 ppm			
Streptomycin	17	18	15	17	13	14	18	20	34	36	35	37	-	-	-	-			
Redomil	-	-	-	-	-	-	-	-	-	-	-	-	90	100	88	100			
H ₂ L ₁	5	10	6	12	7	8	6	8	10	11	7	8	26	31	30	32			
H ₂ L ₂	6	10	8	14	8	9	9	10	11	13	8	9	27	33	29	35			
H ₂ L ₃	8	11	13	15	9	10	11	13	13	15	10	12	28	35	35	37			
(i)	11	15	12	13	7	9	11	15	20	23	25	26	71	75	68	78			
(ii)	13	16	12	14	8	10	13	16	22	25	26	28	73	77	70	80			
(iii)	14	16	13	14	9	10	13	17	25	28	28	30	75	79	71	82			
(iv)	14	15	14	15	11	12	14	18	27	30	28	32	76	81	74	80			
(v)	15	16	14	16	11	13	15	19	29	32	29	33	79	80	76	81			
(vi)	15	16	15	16	12	13	16	19	30	33	32	35	81	86	78	88			
(vii)	12	15	12	13	9	11	13	16	25	26	28	29	73	78	70	79			
(viii)	13	14	13	14	10	11	14	16	26	28	29	30	75	80	72	82			
(ix)	14	15	15	15	11	12	15	18	28	30	30	31	78	82	75	85			

The band at $1530\text{--}1550\text{ cm}^{-1}$ has been assigned to the $\nu(\text{C}\cdots\text{O})$ ¹⁹.

Electrochemical studies : Electrochemical measurements on complexes (i)–(ix) in DMF, containing tetrabutylammoniumperchlorate (TBAP), at a glassy carbon electrode (GCE) showed three one-electron redox couples in the potential range 0.7 to -1.4 V vs saturated calomel electrode (SCE). The couple appearing at positive potentials (0.4–0.56 V) is assigned to the metal centered redox couple $\text{Ru}^{\text{V}}/\text{Ru}^{\text{IV}}$, while the other two are assigned to the $\text{Ru}^{\text{IV}}/\text{Ru}^{\text{III}}$ and $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ couples, respectively. Most of the ruthenium(III) complexes also showed an irreversible ligand-based anodic oxidation wave in the range $+0.9$ to $+1.1\text{ V}$ when the anodic scans were further extended. This is an indication of significant stabilization of the ruthenium(III) state in these complexes.

Thermal studies : The presence of outer chloride ion in all complexes, one water molecule (in complexes (iv), (v) and (vi)) or two molecule of water (in complexes (i), (ii) and (iii)) and a molecule of diamine and ethanol (in complexes (vii), (viii) and (ix)) are confirmed by TG studies. The TG curves were studied in the $30\text{--}700\text{ }^{\circ}\text{C}$ range and showed that the thermal decomposition of the complexes takes place in several steps. It is possible that different groups in the ligands lead to a decrease in the stability of all the complexes. Furthermore, it is known that the electronegativity and the atomic radius of the central metal atom also affect the thermal stability.

Quantitative antimicrobial assay : The results (Table 3) of antimicrobial screening have been compared with the conventional bactericide streptomycin and fungicide redomil, taken as standard in each case. It is evident that although the H_2L_1 , H_2L_2 and H_2L_3 ligands alone were quite toxic, their activity increased upon complexation²⁰. The increase in the antimicrobial activity of metal chelates with increase in concentration is due to the effect of metal ion on the normal cell process. Such increased activity of the metal chelates can be explained on the basis of Overtone's concept and chelation theory²¹.

According to Overtone's concept of cell permeability, the lipid membrane that surrounds the cell favours the passage of only lipid soluble materials due to which con-

trols the antimicrobial activity. After chelation, the polarity of the metal ion will be reduced to a greater extent due to the overlap of the ligand orbital and partial sharing of positive charge of metal ion with donor groups. Further, it increases the delocalisation of π -electrons over the whole chelate ring and enhances the lipophilicity of the complexes. This increased lipophilicity enhances the penetration of the complexes into lipid membrane and blocking the metal binding sites on enzymes of microorganism. These complexes also disturb the respiration process of the cell and thus block the synthesis of proteins, which restrict the further growth of the organism. Furthermore, the mode of action of the compounds may involve formation of hydrogen bond through azomethine group with the active centers of cell constituents, resulting in interference with the normal cell process²².

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