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Studies on the synthesis, spectra, catalytic and antibacterial activities of binuclear ruthenium(II) complexes

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ABSTRACT

A new series of stable binuclear ruthenium(II) carbonyl complexes of the general formula [{RuX(CO)(EPh$_3$)$_2$}$_2$L] (where X = H or Cl; E = P or As and L = dibasic tetradentate diacetyl resorcinol (H_2-DAR)) have been synthesised by reacting ruthenium(II) starting complexes [RuHX(CO)(EPh$_3$)$_3$] (where X = H or Cl; E = P or As) and 4,6-diacetylresorcinol (H_2-DAR) ligand in benzene medium. The structure of the new binuclear ruthenium(II) carbonyl complexes was established using elemental analysis, spectra (FT-IR, UV–vis and ^{1}H NMR), electrochemical and thermal studies. In these reactions, the 4,6-diacetylresorcinol (H_2-DAR) ligand behaves as a binegative tetradentate chelating ligand coordinating through O,O atoms of both the carbonyl and phenolic C–O groups by replacing a molecule of PPh$_3$/AsPh$_3$ and a hydride ion from the starting complexes. Further, all these complexes were also employed as new catalysts for the oxidation of primary and secondary alcohols in the presence of N-methylmorpholine-N-oxide (NMO) as a more viable co-oxidant. The free ligand and their metal complexes have also been screened for their antibacterial activity against the growth of gram +ve and gram −ve bacterial cultures.

1. Introduction

Studies on the coordination chemistry of binuclear transition metal complexes have received much attention in recent years [1,2]. Bimetallic coordination compounds serve as model systems for variety of biological reactions such as oxygen transport [3], oxygen activation, photocatalytic water splitting [4], electron transfer process [5], metal–metal interaction, etc. The presence of two metal ions in close proximity can lead to a spin-exchange and unusual magnetic properties. The proximity of another metal ion in the same molecule can modify the redox properties of each metal centers and hence affect the catalytic activity of the metal complexes [6]. In the use of transition metal carbonyls as reactive species in the homogeneous catalytic reactions such as hydrogenation, hydroformylation and carbonylation, carbon monoxide serves simply as ligand providing the complex with the necessary reactivity and stability to allow reaction [7]. The accessibility of ruthenium higher oxidation states [8,9] converts them into excellent candidates for catalytic redox reactions.

Among the different catalytic processes, the one involving the oxidation of primary and secondary alcohols into their corresponding aldehydes and ketones plays a central role in organic synthesis [10,11]. From both an economic and environmental point of view, the quest for effective catalytic systems that use clean, inexpensive primary oxidants such as molecular oxygen or hydrogen peroxide, i.e., a green method for converting alcohols to carbonyl compounds on an industrial scale remains an important challenge [12]. Most studies of alcohol oxidation using both homogeneous and heterogeneous catalysts involve the use of group VIII metal complexes. Ruthenium compounds such as $RuCl_3$ and some other high valent oxoruthenium complexes have been extensively investigated as catalyst for alcohol oxidation using variety of primary oxidants like iodobenzene, NMO [13], tert-hydroperoxide [14], hypochloride [15], bromate or a combination of oxygen and an aldehyde.

Reports on the oxidation of cholesterol, geraniol, etc., catalysed by ruthenium complexes in the presence of NMO and N,N-dimethylaniline-N-oxide were reported in the literature [16] and the catalytic activities of ruthenium complexes containing tertiary phosphine and arsine ligands are well established [17,18]. In addition, the presence of ruthenium–halogen bonds in several ruthenium complexes exhibiting anticancer activity suggests that these bonds may also play some important role [19]. Further, there has been an upsurge of interest in the chemistry of transition metal chelates containing O,O; O,N; N,S and S,S donor ligands due to their potential carcinostatic, antitumour, antifungal, antiviral and antibacterial activities [20–22].

This article deals with the study of coordination behaviour of 4,6-diacetylresorcinol (H_2-DAR) towards the ruthenium(II) complexes containing triphenylphosphine and triphenylarsine. The structure of new binuclear ruthenium(II) carbonyl complexes

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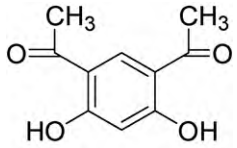


Fig. 1. Structure of 4,6-diacetylresorcinol (H_2-DAR) ligand.

obtained has been proposed on the basis of elemental analysis, UV–visible, IR, ^{1}H NMR, electrochemical and thermal studies. From the application point of view, catalytic and antibacterial activities of the new binuclear ruthenium(II) carbonyl complexes have also been carried out.

2. Experimental

2.1. Materials and reagents

Resorcinol, acetic anhydride and zinc chloride were Merck chemicals. $RuCl_3{\cdot}3H_2O$ was purchased from Loba Chemie Pvt Ltd. N-methylmorpholine-N-oxide was purchased from Aldrich. All the reagents used were chemically pure and analar grade. Solvents were purified and dried according to standard procedures [23].

2.2. Physical measurements

Microanalysis of carbon and hydrogen was carried out using Vario EL III CHNS analyser. The IR spectra of the ligand and their complexes were recorded as KBr pellets on a Nicolet Avatar model in 4000–400 cm^{-1} range. Electronic spectra of the metal complexes were recorded on a Jasco UV–vis spectrophotometer using dichloromethane as a solvent. The ^{1}H NMR spectra of the ligand (H_2-DAR) and ruthenium(II) complexes were recorded on a Bruker 400 MHz instrument at room temperature using $CDCl_3$ as a solvent and TMS as an internal standard. Thermal analysis of the complexes has been carried out by using NETZSCH Gerateban Bestell-Nr 348472C. Electrochemical measurements were made using a CH Instruments electrochemical analyser. Melting points were recorded using Raaga apparatus and were uncorrected.

The starting complexes $[RuHCl(CO)(PPh_3)_3]$ [24], $[RuHCl(CO)(AsPh_3)_3]$ [25], $[RuH_2(CO)(PPh_3)_3]$ [25] and $[RuH_2(CO)(AsPh_3)_3]$ [26] were prepared according to the literature reports.

2.3. Synthesis of 4,6-diacetylresorcinol ligand (H_2-DAR) [27]

Acetylation of resorcinol (5 g; 45.5 mmol) with acetic anhydride (9.28 g; 91.0 mmol) using excess zinc chloride (10.0 g; 73.4 mmol) was carried out at 140 °C in a paraffin oil bath. After 5 h, the hot mixture was cooled to room temperature and poured onto 140 ml of 50% dil. HCl and the orange precipitate formed was allowed to stand for an hour. The crude product was filtered, washed several times with distilled water and further purified by column chromatography using petroleum ether and ethyl acetate mixture (95:5) which yielded colourless compound (Fig. 1) (yield: 78%, M.P.: 179 °C).

2.4. Synthesis of the new metal complexes

All the new metal complexes were prepared according to the following general procedure. To a boiling solution of 4,6-diacetylresorcinol (H_2-DAR) (0.0194 g; 0.1 mmol) (L) in benzene, few drops of triethylamine was added, followed by the addition of $[RuHCl(CO)(PPh_3)_3]$ (0.190 g; 0.2 mmol), $[RuHCl(CO)(AsPh_3)_3]$ (0.216 g; 0.2 mmol), $[RuH_2(CO)(PPh_3)_3]$ (0.183 g; 0.2 mmol), $[RuH_2(CO)(AsPh_3)_3]$ (0.202 g; 0.2 mmol) in benzene refluxed for 8 h. Then the resulting solution was concentrated to 5 ml and the product precipitated by the addition of petroleum ether (60–80 °C) was recrystallised using CH_2Cl_2. The compounds were dried under vacuum and the purity of the complexes was checked by TLC. Our sincere effort to obtain single crystals of the complexes went unsuccessful.

2.5. Catalytic oxidation

The catalytic activity of the above complexes for the oxidation of benzyl alcohol and cyclohexanol to benzaldehyde and cyclohexanone was tested in the presence of NMO as a co-oxidant. In a typical reaction, binuclear ruthenium(II) complexes were used as a catalyst and primary and secondary alcohols namely benzyl alcohol, cyclohexanol were used as substrates at 1:200 molar ratio as described bellow.

To a solution of the respective substrates (1 mmol) in CH_2Cl_2, N-methylmorpholine-N-oxide (3 mmol) and a solution of ruthenium complex (0.005 mmol) in the same solvent were added and refluxed for 3 h. The solvent was then evaporated to dryness under reduced pressure and the residue thus obtained was then extracted thrice with petroleum ether (60–80 °C) (20 ml) and the combined extract was evaporated to yield corresponding aldehyde or ketone which was then quantified as 2,4-dinitrophenylhydrazone derivative [28]. The catalytic activity of the complex was determined from the percent yield (Y%) and the turnover (T.O.) conversion of alcohol to aldehyde or ketone is as follows:

$$Y(\%) = \frac{\text{weight of alcohol oxidised to aldehyde or ketone}}{\text{total weight of alcohol}} \times 100$$

$$\text{T.O.} = \frac{\text{millimoles of product}}{\text{millimoles of catalyst}}$$

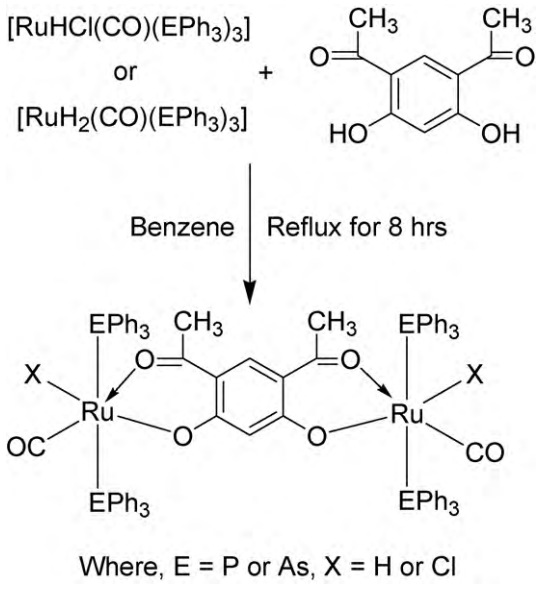
2.6. Antibacterial activity

The *in vitro* antibacterial screening of the ligand (H_2-DAR) and the corresponding binuclear ruthenium(II) carbonyl complexes have been carried out against human pathogenic bacteria such gram positive (*Staphylococcus aureus*) and gram negative (*Klebsiella pneumoniae* and *Escherichia coli*) using disc diffusion method. The test organisms were grown on nutrient agar medium in petriplates. Triplicate plates were maintained in the antibacterial assays. The compounds to be tested were dissolved in DMSO to a final concentration of 0.10%, 0.25%, 0.50% and 1.0% and soaked in filter paper disc of 5 mm diameter and 1 mm thickness. These discs were placed on the previously seeded plates and incubated at 37 °C for 24 h. The diameter (mm) of inhibition zone around each disc was determined after 24 h. Streptomycin was used as a standard.

3. Results and discussion

Binuclear ruthenium(II) carbonyl complexes of the composition $[\{RuX(CO)(EPh_3)_2\}_2L]$ (where X = H or Cl; E = P or As and L = dibasic tetradentate 4,6-diacetylresorcinol ligand (H_2-DAR)) were synthesised in quantitative yield from the reactions of $[RuHX(CO)(EPh_3)_3]$ (where X = H or Cl; E = P or As) with H_2-DAR ligand in 2:1 molar ratio in dry benzene as shown in Scheme 1.

The prepared complexes are listed in Table 1 together with their elemental analysis and colour. The complexes are green or brown in colour and the proposed structure of the complexes are in good agreement with the stoichiometries concluded from their analytical data. All the complexes are stable in air at room temperature, non-hygroscopic in nature and are soluble in most common organic solvents such as CH_2Cl_2, $CHCl_3$, C_6H_6, CH_3CN, DMSO and DMF. In all the reactions, the H_2-DAR behaves as a binegative tetradentate chelating ligand through O,O atoms of both the carbonyl C=O and



Scheme 1.

phenolic C–O by replacing one molecule of PPh_3/$AsPh_3$ and one molecule of hydride ion from the starting monomeric complexes.

3.1. Infrared spectra

A comparison between the IR spectral data of the free ligand and the metal complexes was made to study the binding mode of the H_2-DAR to the ruthenium ion in the new metal complexes. Some of the important infrared absorption bands of H_2-DAR ligand and the complexes are shown in Table 2.

In the infrared spectra of the free ligand, a strong band characteristic of carbonyl (>C=O) group is observed at 1657 cm^{-1}. Coordination of the H_2-DAR ligand to the metal through carbonyl oxygen atom is expected to reduce the electron density in the carbonyl link and lower the $\nu_{(C=O)}$ absorption frequency. In the spectra of all the new complexes, a considerable decrease in the frequency of the above functional group was observed and appeared in the 1601–1595 cm^{-1} region, indicating the coordination of the carbonyl oxygen (>C=O) to ruthenium metal [29]. Another medium intensity band appeared around 3415 cm^{-1} in the spectra of free ligand due to $\nu_{(OH)}$ was absent in the spectra of the complexes indicating the deprotonation of H_2-DAR ligand prior to coordination [30].

This fact is further supported by the increase in phenolic C–O stretching frequency from 1251 cm^{-1} in the ligand to 1322–1316 cm^{-1} in the complexes which indicates the other coordination site of H_2-DAR ligand is phenolic oxygen [28,31]. Also, the existence of a strong band in the region of 1939–1936 cm^{-1} in the spectra of all the complexes reveals that the presence of terminally coordinated carbon monoxide [32]. In addition to the above, other characteristic bands due to PPh_3/$AsPh_3$ were also present in the expected regions for the complexes.

3.2. Electronic spectra

All the new binuclear ruthenium(II) carbonyl complexes have been found to be diamagnetic indicating the presence of ruthenium in the +2 oxidation state (t_{2g}^6 configuration). The ground state of ruthenium(II) in an octahedral environment is $^1A_{1g}$ arising from the t_{2g}^6 configuration. The excited states corresponding to t_{2g}^5 e_g^1 configuration are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$, $^1T_{2g}$. Hence, four bands corresponding to the transitions $^1A_{1g} \rightarrow {}^3T_{1g}$, $^1A_{1g} \rightarrow {}^3T_{2g}$, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ are possible in the order of increasing energy. Electronic spectra of all the complexes in dichloromethane showed two bands in the region of 340–275 nm (Table 2). The band in the 330–340 nm range has been assigned to the spin allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transition which is in confirmity with the assignments made earlier for other similar octahedral ruthenium(II) complexes [33,34]. The other high intensity bands in the region 270–280 nm have been assigned to the charge transfer transition arising from the excitation of an electron from the metal t_{2g} level to the unfilled molecular orbitals derived from the π^* level of the ligands [33–36].

3.3. ^1H NMR spectra

The ^1H NMR spectra of the H_2-DAR and the corresponding binuclear ruthenium(II) carbonyl complexes were recorded in $CDCl_3$ to confirm the presence of coordinated ligand in the complexes. The data and their assignments are listed in Table 3.

In the ^1H NMR spectrum of the ligand, a sharp singlet was observed at 12.8 ppm due to hydroxylic –OH protons (with an integration corresponding to two protons). But the spectra of all

Table 1
Physico-chemical and analytical data of H_2-DAR and binuclear ruthenium(II) carbonyl complexes.

Ligand/complex	Empirical formula	Colour	M.P. (°C)	Found (calculated) (%)	
				C	H
H_2-DAR	$C_{10}H_{10}O_2$	White	179	–	–
[{RuCl(CO)$(PPh_3)_2$}$_2$L]	$C_{84}H_{68}O_6Cl_2P_4Ru_2$	Green	182	63.68 (64.24)	4.12 (4.36)
[{RuCl(CO)$(AsPh_3)_2$}$_2$L]	$C_{84}H_{68}O_6Cl_2As_4Ru_2$	Brown	178	56.90 (57.78)	3.02 (3.92)
[{RuH(CO)$(PPh_3)_2$}$_2$L]	$C_{84}H_{70}O_6P_4Ru_2$	Green	212	67.02 (67.19)	4.58 (4.69)
[{RuH(CO)$(AsPh_3)_2$}$_2$L]	$C_{84}H_{70}O_6As_4Ru_2$	Brown	206	59.56 (60.15)	3.76 (4.20)

Table 2
Characteristic infrared frequencies and electronic spectral data of H_2-DAR ligand and binuclear ruthenium(II) carbonyl complexes.

Ligand/complex	$\nu_{(O-H)}$	$\nu_{(C=O)}$	$\nu_{(Ph-CO)}$	$\nu_{(Ru-CO)}$	λ_{max} (nm)
H_2-DAR	3415	1657	1251	–	–
[{RuCl(CO)$(PPh_3)_2$}$_2$L]	–	1601	1320	1938	340[a], 275[b]
[{RuCl(CO)$(AsPh_3)_2$}$_2$L]	–	1601	1316	1937	330[a], 278[b]
[{RuH(CO)$(PPh_3)_2$}$_2$L]	–	1598	1320	1936	335[a], 280[b]
[{RuH(CO)$(AsPh_3)_2$}$_2$L]	–	1595	1322	1939	338[a], 276[b]

ν is in units of cm^{-1}.
[a] $^1A_{1g} \rightarrow {}^1T_{1g}$.
[b] Charge transfer.

Table 3
^{1}H NMR data of H_2-DAR ligand and binuclear ruthenium(II) carbonyl complexes.

Ligand/complex	^{1}H NMR data (ppm)
H_2-DAR	12.8 (–OH, s), 6.3 and 8.1 (Ar, s), 2.5 (–$COCH_3$, s)
[{RuCl(CO)(PPh_3)$_2$}$_2$L]	6.5–8.2 (a, m), 2.6 (–$COCH_3$, s)
[{RuCl(CO)($AsPh_3$)$_2$}$_2$L]	6.2–8.2 (a, m), 2.7 (–$COCH_3$, s)
[{RuH(CO)(PPh_3)$_2$}$_2$L]	6.4–8.2 (a, m), 2.7 (–$COCH_3$, s)

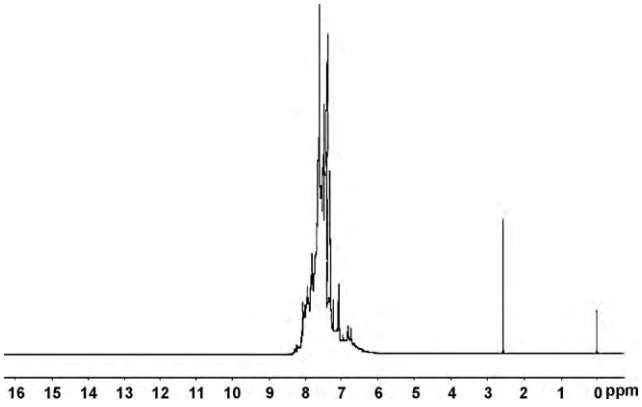
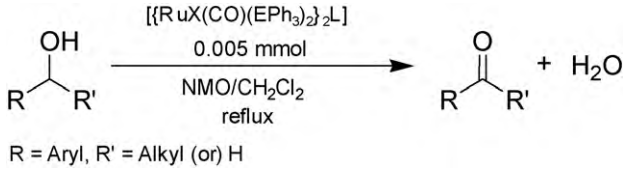


Fig. 2. ^{1}H NMR spectrum of [{RuCl(CO)(PPh_3)$_2$}$_2$L] complex.

the metal complexes (Fig. 2) showed no signal at around 12 ppm due to the hydroxylic proton, which revealed that the hydroxyl group underwent deprotonation prior to the coordination with ruthenium ion [34,37]. The signals observed at 8.1 and 6.3 ppm in the spectrum of the free ligand were due to aromatic protons and another sharp singlet at 2.5 ppm in the ligand is assigned for the methyl protons of –$COCH_3$ group. In the spectra of the complexes, the signal due to methyl protons of –$COCH_3$ group has been observed around 2.6–2.7 ppm as a singlet and the characteristic multiplets of the PPh_3/$AsPh_3$ and the aromatic protons were appeared in the range of 6.2–8.2 ppm.

3.4. Thermogravimetric analysis

Thermal gravimetric analysis (TGA) was used as a probe to prove the presence of associated water or solvent molecules in the coordination sphere or in the crystal lattice [38]. The thermal gravimetric analysis was carried out for two of the complexes [{RuCl(CO)(PPh_3)$_2$}$_2$L] and [{RuCl(CO)($AsPh_3$)$_2$}$_2$L] in the range of about 50–800 °C and it showed that the thermal decomposition of the complexes takes place in several steps. The thermal analysis data of the ruthenium(II) complexes indicates that they are stable up to 200 °C owing to their anhydrous nature. DTA curves show no endothermic peaks up to 200 °C confirming the absence of lattice or coordinated water molecules in the complexes [14,39]. A sharp decomposition corresponding to the loss of organic moiety (85–86.5%) was observed in the temperature range of 350–400 °C beyond which no decomposition was observed indicating the formation of stable ruthenium oxide.



Scheme 2.

3.5. Electron transfer properties

Dichloromethane solutions of the complexes have been used to study the electron transfer properties with the help of cyclic voltammetry and the data are presented in Table 4. All the complexes are redox active and in each case, the one electron stoichiometry of the observed responses is confirmed by comparing the current heights with reported values of one electron redox process [40–42]. All the diruthenium complexes showed two successive responses for quasi-reversible oxidation and the well defined half wave potentials $E_{1/2}$ in the range 1.05–1.07 V correspond to the first oxidation response and the second oxidation response in the range 0.44–0.55 V. The responses observed for complexes are assigned to the metal centered Ru(II)Ru(II) to Ru(III)Ru(II) and Ru(III)Ru(II) to Ru(III)Ru(III) oxidation process.

$$\text{Ru(II)–Ru(II)} \underset{E_{1/2}\,(\text{oxd1})}{\overset{-e^-}{\rightleftharpoons}} \text{Ru(III)–Ru(II)} \underset{E_{1/2}\,(\text{oxd2})}{\overset{-e^-}{\rightleftharpoons}} \text{Ru(III)–Ru(III)}$$

From all the above facts, it is concluded that all the diruthenium complexes did not show any reduction responses at negative potentials [43]. The redox potentials are independent of the various scan rates and support the quasi-reversible responses. It has also been observed that there is no much variation in the redox potentials of the complexes due to the substitution of triphenylphosphine by triphenylarsine.

3.6. Catalytic oxidation

The applications of diruthenium complexes as an inexpensive and easy to handle co-oxidant for selective oxidation of alcohols are well known in the literature [44,45]. No oxidation of alcohols to their corresponding aldehydes and ketones was achieved in our case by employing NMO only. Thus, the catalytic oxidation of benzyl alcohol to benzaldehyde and cyclohexanol to cyclohexanone by the precursor catalyst [{RuX(CO)(EPh_3)$_2$}$_2$L] (where X = H or Cl; E = P or As and L = H_2-DAR) in the presence of NMO in 1:200 molar ratio of catalyst to substrate at room temperature in dry CH_2Cl_2 was carried out (Scheme 2). Good experimental yield with appreciable turnover of benzyl alcohol to benzaldehyde and cyclohexanol to cyclohexanone (Table 5) was achieved using the newly synthesised ruthenium(II) complexes similar to that of other ruthenium(II) complexes reported elsewhere [46,47]. The formation of benzaldehyde and cyclohexanone was confirmed by the formation of 2,4-dinitrophenylhydrazone.

The possible mechanism for the catalytic oxidation of alcohols to carbonyl compounds in the presence of co-oxidant could be pro-

Table 4
Cyclic voltammetric data of binuclear ruthenium(II) carbonyl complexes.

Complex	$Ru_2^{III,III}$–$Ru_2^{II,II}$							
	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (mV)	E_{pa} (V)	E_{pc} (V)	$E_{1/2}$ (V)	ΔE_p (mV)
[{RuCl(CO)(PPh_3)$_2$}$_2$L]	1.12	1.01	1.06	110	0.64	0.45	0.55	190
[{RuCl(CO)($AsPh_3$)$_2$}$_2$L]	1.13	0.98	1.05	150	0.51	0.37	0.44	140
[{RuH(CO)(PPh_3)$_2$}$_2$L]	1.12	1.02	1.07	100	0.56	0.41	0.49	150
[{RuH(CO)($AsPh_3$)$_2$}$_2$L]	1.14	1.00	1.07	140	0.57	0.39	0.48	180

Table 5
Data for catalytic oxidation of alcohols using binuclear ruthenium(II) carbonyl complexes in the presence of NMO.

Complex	Substrate	Product	Yield[a] (%)	TON[b]
$[\{RuCl(CO)(PPh_3)_2\}_2L]$	Benzyl alcohol	Benzaldehyde	71.93[c]	148.92
	Cyclohexanol	Cyclohexanone	45.60[c]	95.25
$[\{RuCl(CO)(AsPh_3)_2\}_2L]$	Benzyl alcohol	Benzaldehyde	70.30[c]	145.80
	Cyclohexanol	Cyclohexanone	43.03[c]	89.88
$[\{RuH(CO)(PPh_3)_2\}_2L]$	Benzyl alcohol	Benzaldehyde	69.95[c]	145.07
	Cyclohexanol	Cyclohexanone	42.78[c]	89.36
$[\{RuH(CO)(AsPh_3)_2\}_2L]$	Benzyl alcohol	Benzaldehyde	71.17[c]	147.60
	Cyclohexanol	Cyclohexanone	43.49[c]	90.84

[a] Yield based on substrate: alcohol (1 mmol); NMO (3 mmol); catalyst (0.005 mmol).
[b] Ratio of moles of product obtained to the moles of the catalyst used.
[c] Estimated as 2,4-dinitrophenylhydrazone derivative.

Table 6
Antibacterial activity data of binuclear ruthenium(II) carbonyl complexes.

Ligand/complex	Diameter of inhibition zone (mm)											
	S. aureus				*Klebsiella pneumoniae*				*E. coli*			
	0.10%	0.25%	0.50%	1.0%	0.10%	0.25%	0.50%	1.0%	0.10%	0.25%	0.50%	1.0%
H_2-DAR	2 (±0.3)	5 (±1.8)	6 (±0.5)	7 (±1.1)	4 (±1.1)	5 (±0.6)	7 (±0.8)	7 (±0.8)	4 (±0.5)	4 (±0.8)	5 (±0.8)	7 (±0.8)
1	6 (±0.8)	9 (±0.8)	15 (±0.5)	20 (±0.8)	7 (±0.8)	14 (±1.4)	18 (±0.6)	20 (±0.5)	9 (±0.5)	10 (±0.5)	13 (±0.8)	16 (±1.2)
2	8 (±0.8)	10 (±0.5)	14 (±0.8)	20 (±0.5)	8 (±0.8)	10 (±0.8)	14 (±1.2)	17 (±1.4)	7 (±0.8)	11 (±1.7)	18 (±1.5)	20 (±0.5)
3	8 (±2.0)	10 (±0.8)	15 (±0.5)	18 (±0.6)	10 (±0.8)	15 (±0.5)	19 (±0.5)	20 (±0.5)	7 (±0.5)	8 (±0.5)	14 (±1.1)	20 (±0.8)
4	9 (±0.5)	12 (±0.8)	13 (±0.5)	16 (±1.4)	9 (±0.5)	14 (±0.5)	18 (±0.5)	22 (±0.8)	9 (±0.3)	12 (±0.3)	15 (±0.3)	19 (±0.5)
S	13 (±0.4)	18 (±0.9)	21 (±1.3)	25 (±0.5)	11 (±0.6)	17 (±1.5)	22 (±0.8)	26 (±2.0)	12 (±0.5)	17 (±1.1)	23 (±1.8)	26 (±0.7)

1: $[\{RuCl(CO)(PPh_3)_2\}_2L]$; 2: $[\{RuCl(CO)(AsPh_3)_2\}_2L]$; 3: $[\{RuH(CO)(PPh_3)_2\}_2L]$; 4: $[\{RuH(CO)(AsPh_3)_2\}_2L]$; S: streptomycin.

ceeded via the formation of μ-peroxoruthenium(IV) intermediate species [47] that are capable to abstract hydrogen atom from the –OH group in alcohol.

3.7. Antibacterial activity

The *in vitro* antibacterial screening of the ligand (H_2-DAR) and their binuclear ruthenium(II) carbonyl complexes has been carried out against human pathogenic bacteria such as gram positive (*S. aureus*) and gram negative (*K. pneumoniae* and *E. coli*) using disc diffusion method [48]. Triplicate plates were maintained in the antibacterial assays. The compounds to be tested were dissolved in DMSO to a final concentration of 0.10%, 0.25%, 0.50% and 1.0%. The standard error for each assay is presented in the parentheses. From the results given in Table 6, it has been observed that the ruthenium complexes showed better activity than the free ligand under identical experimental conditions. The possible mode of increased toxicity of the ruthenium complexes compared to that of free ligand may be explained in terms of Tweedy's theory [49], according to this, chelation reduces the polarity of the metal atom because of partial sharing of its positive charge with a donor group and possible π-electron delocalization over the whole chelate ring. Such a chelation could enhance the lipophilic character of the central metal atom, which subsequently favors its permeation through the lipid layers of the cell membrane [50] and blocking the metal binding sites on enzymes of microorganism. The variation in the effectiveness of the different compounds against different organisms depends on their impermeability of the microbial cells or on the difference in the ribosome of the microbial cells [51]. These complexes also disturb the respiration process of the cell and block the synthesis of proteins which restrict the further growth of the organism. The inhibition of the activity of the compounds increases with increase in the concentration. Though there is a marked increase in the bacterial activity of ruthenium complexes as compared to the free ligand, it could not reach the effectiveness of streptomycin [52].

4. Conclusion

Binuclear ruthenium(II) carbonyl complexes of the composition $[\{RuX(CO)(EPh_3)_2\}_2L]$ (where X = H or Cl; E = P or As and L = dibasic tetradentate diacetyl resorcinol (H_2-DAR)) have been prepared by reacting ruthenium(II) starting complexes $[RuHX(CO)(EPh_3)_3]$ (where X = H or Cl; E = P or As) with 4,6-diacetylresorcinol (H_2-DAR) ligand under reflux conditions. The new complexes obtained were characterised on the basis of elemental analysis, spectra (FT-IR, UV–vis and ^{1}H NMR), electrochemical and thermal studies. The catalytic efficiency of these complexes towards the oxidation of primary and secondary alcohols into their corresponding carbonyl compounds showed some promising results. *In vitro* antibacterial screening revealed that these complexes are effective against both gram +ve and gram −ve pathogenic bacteria.

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