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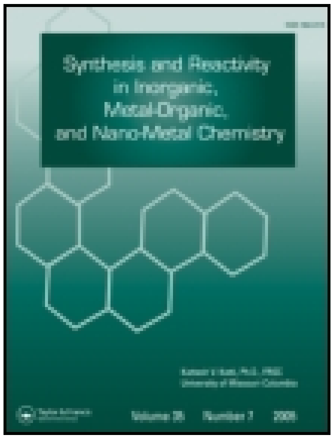

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SYNTHESIS AND BIOLOGICAL ACTIVITY OF RUTHENIUM(II) CARBONYL COMPLEXES CONTAINING TETRADENTATE SCHIFF BASES

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SYNTHESIS AND BIOLOGICAL ACTIVITY OF RUTHENIUM(II) CARBONYL COMPLEXES CONTAINING TETRADENTATE SCHIFF BASES

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ABSTRACT

Several hexa-coordinated ruthenium(II) carbonyl complexes of the type [Ru(CO)(B)(L)] (B = PPh_3, pyridine (py), piperidine (pip) or morpholine (morph); H_2L = tetradentate Schiff bases) have been prepared by the reactions of [RuHCl(CO)(PPh_3)$_2$(B)] (B = PPh_3 or py or pip or morph) with appropriate Schiff bases having the donor groups O,N *viz.*, *o*-hydroxyacetophenoneethylenediimine, H_2(*o*-hyacen); *o*-hydroxyacetophenonepropylenediimine, H_2(*o*-hyacpn); *o*-hydroxyacetophenonetetramethylenediimine, H_2(*o*-hyactn), and *o*-hydroxyacetophenone-*ortho*-phenylenediimine, H_2(*o*-hyacopn), in 1:1 molar ratio. The complexes have been characterised on the basis of elemental analyses and spectral (IR, electronic, ^{1}H and ^{31}P NMR) data. The antibacterial activities of these new complexes were also tested.

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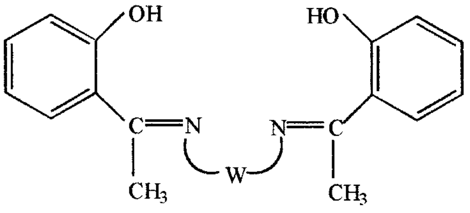
INTRODUCTION

Among the platinum group metals, ruthenium has been studied extensively in terms of its coordination and organometallic chemistry. Electron transfer reactions are fundamental and play an important role in chemical and biological processes.[1] Although there is a wealth of information available on transition metal complexes of Schiff bases,[2] it is largely confined to the first row transition metals, notably iron, cobalt and nickel.[3,4] Very little has been reported for the Schiff base complexes of ruthenium. In recent years, the continued interest in ruthenium complexes is due to their importance in catalytic oxidative processes.[5] In view of the growing interest in oxygenation and carboxylations of ruthenium(II) complexes as new catalysts, we report in the present communication the synthesis and characterisation of some stable ruthenium(II) Schiff base carbonyl complexes of the type [Ru(CO)(L)(B)] (B = PPh_3 or pyridine (py) or piperidine (pip) or morpholine (morph); H_2L = tetradentate Schiff bases). It is of special interest to study the effect of electron donating substituents on the Schiff base ligand on the antibacterial activities of ruthenium(II) complexes that are formed from them. The general structures of the Schiff base ligands used in the present study are shown in Fig. 1.



W	Acronym
$-(CH_2)_2-$	H_2(*o*-hyacen)
$-(CH(CH_3)-CH_2-)-$	H_2(*o*-hyacpn)
$-(CH_2)_4-$	H_2(*o*-hyactn)
$-(C_6H_4)-$	H_2(o-hyac*o*pn)

Figure 1. Structures of the ligands.

EXPERIMENTAL

$RuCl_3 \cdot 3H_2O$ was purchased from Loba-Chemie and used without further purification. All the reagents were of Analar or chemically pure grade. The solvents were purified and dried according to standard procedures.[6] IR spectra were recorded with a Shimadzu FTIR-8200 spectrophotometer in the range 4000–500 cm^{-1}. Electronic spectra were recorded in CH_2Cl_2 on a Hitachi-Elmer Model 20/200 spectrophotometer. Melting points were recorded on a micro heating table and are uncorrected. Elemental analyses were carried out using Carlo Erba 1106 and Perkin-Elmer Model 240 CHN analysers at the Central Drug Research Institute, Lucknow, India. ^1H and ^{31}P NMR spectra were recorded on Brucker 400 MHz or Varian FX 90 Q instruments using TMS as an internal reference and Brucker WM 400 MHz instruments using *ortho*-phosphoric acid as a reference, respectively, at the Indian Institute of Science, Bangalore, India. The antibacterial activity studies were carried out at the Department of Environmental Sciences, Bharathiar University, Coimbatore, India. The starting complexes, $[RuHCl(CO)(PPh_3)_3]$ and $[RuHCl(CO)(PPh_3)_2(B)]$ (where B = py or pip or morph), and the ligand have been prepared according to published procedures.[7,8]

Preparation of the Complexes

To a solution of $[RuHCl(CO)(PPh_3)_2(B)]$ ($B = PPh_3$ or py or pip or morph) (0.11–0.13 g, 0.1 mmol) in benzene (25 mL), was added the appropriate tetradendate Schiff base ligand (0.013–0.014 g, 0.1 mmol) (molar ratio of ruthenium complex:Schiff base ligand = 1:1). The mixture was heated under reflux for 5 h. The resulting dark coloured solution was then concentrated to about 3 mL and the product was separated out by the addition of a small quantity of petroleum ether (60–80 °C). The complexes were filtered and recrystallised from CH_2Cl_2/petroleum ether (1:10). The purity of the complexes was checked by TLC. Yields, 70–80%.

RESULTS AND DISCUSSION

Ruthenium(II) carbonyl complexes [Ru(CO)(B)(L)] ($B = PPh_3$ or pyridine (py) or piperidine (pip) or morpholine (morph); H_2L = tetradentate Schiff bases) have been synthesised by the reactions of $[RuHCl(CO)(PPh_3)_2(B)]$ (where $B = PPh_3$ or py or pip or morph) with the appropriate Schiff bases having the donor groups O,N in 1:1 molar ratio.

$$[\mathrm{RuHCl(CO)(PPh_3)_2(B)}] + \mathrm{H_2L} \longrightarrow [\mathrm{Ru(CO)(B)(L)}]$$

The analytical data (Table I) are in good agreement with the general molecular formulas and all the complexes are quite stable in air and light. The new products obtained from the reactions of [RuHCl(CO)(PPh_3)$_3$] with

Table I. Analytical Data of Ruthenium(II) Complexes

Complex	Yield (%)	Colour	M. p. (°C)	Found (Calcd.) % C	H	N
[Ru(CO)(*o*-hyacen)(PPh_3)]	78	Green	147	64.9	4.9	4.1
($C_{37}H_{33}O_3N_2PRu$) (713.78)				(64.8)	(4.9)	(4.1)
[Ru(CO)(*o*-hyacen)(py)]	70	Green	130	57.4	4.7	8.3
($C_{24}H_{23}O_3N_3Ru$) (530.60)				(57.4)	(4.6)	(8.4)
[Ru(CO)(*o*-hyacen)(pip)]	74	Green	120	56.5	5.7	8.3
($C_{24}H_{29}O_3N_3Ru$) (536.64)				(56.7)	(5.7)	(8.3)
[Ru(CO)(*o*-hyacen)(morph)]	70	Brown	125	54.1	5.3	8.3
($C_{23}H_{27}O_4N_3Ru$) (538.61)				(54.1)	(5.3)	(8.2)
[Ru(CO)(*o*-hyacpn)(PPh_3)]	80	Green	110	68.7	5.5	4.1
($C_{38}H_{35}O_3N_2PRu$) (733.77)				(68.6)	(5.5)	(4.1)
[Ru(CO)(*o*-hyacpn)(py)]	75	Green	135	58.9	5.0	7.9
($C_{25}H_{25}O_3N_3Ru$) (550.58)				(58.9)	(5.1)	(7.9)
[Ru(CO)(*o*-hyacpn)(pip)]	71	Green	140	58.1	5.9	7.9
($C_{25}H_{31}O_3N_3Ru$) (556.63)				(58.1)	(6.00)	(7.8)
[Ru(CO)(*o*-hyacpn)(morph)]	70	Brown	127	55.8	5.0	7.8
($C_{24}H_{29}O_4N_3Ru$) (558.60)				(55.8)	(5.0)	(7.8)
[Ru(CO)(*o*-hyactn)(PPh_3)]	70	Green	140	67.2	4.6	3.8
($C_{39}H_{37}O_3N_2PRu$) (685.73)				(67.1)	(4.5)	(3.8)
[Ru(CO)(*o*-hyactn)(py)]	76	Brown	145	60.9	4.3	7.6
($C_{26}H_{27}O_3N_3Ru$) (502.54)				(60.9)	(4.2)	(7.6)
Ru(CO)(*o*-hyactn)(pip)]	77	Green	130	60.3	5.2	7.6
($C_{26}H_{33}O_3N_3Ru$) (508.59)				(60.3)	(5.2)	(7.5)
[Ru(CO)(*o*-hyactn)(morph)]	79	Green	159	58.0	4.9	7.6
($C_{25}H_{31}O_4N_3Ru$) (510.56)				(58.0)	(4.9)	(7.5)
[Ru(CO)(*o*-hyac*o*pn)(PPh_3)]	74	Green	155	65.3	5.0	4.0
($C_{41}H_{33}O_3N_2PRu$) (699.75)				(65.2)	(5.0)	(4.0)
[Ru(CO)(*o*-hyac*o*pn)(py)]	80	Brown	120	58.2	4.9	8.1
($C_{28}H_{23}O_3N_3Ru$) (516.57)				(58.2)	(4.9)	(8.1)
[Ru(CO)(*o*-hyac*o*pn)(pip)]	71	Green	142	57.5	6.0	8.1
($C_{28}H_{29}O_3N_3Ru$) (522.61)				(57.5)	(6.0)	(8.0)
[Ru(CO)(*o*-hyac*o*pn)(morph)]	70	Green	139	55.0	5.6	8.0
($C_{27}H_{27}O_4N_3Ru$) (524.59)				(54.9)	(5.6)	(8.0)

the Schiff bases contained one triphenylphosphine group, (confirmed by ^{31}P NMR spectra), whereas the corresponding reactions with [RuHCl(CO)$(PPh_3)_2$(py)], [RuHCl(CO)$(PPh_3)_2$(pip)] or [RuHCl(CO)$(PPh_3)_2$(morph)] yielded new complexes without triphenylphosphine groups.

IR Spectra

The IR spectra of the Schiff base ligands were compared with those of the ruthenium complexes to obtain information about the binding mode of the ligands to ruthenium in the complexes (Table II). A strong band at 1630–1610 cm^{-1} in the spectra of the free Schiff bases is characteristic of the azomethine (-HC=N-) group. It is expected that coordination of the nitrogen to the metal atom would reduce the electron density in the azomethine link and thus lower the -HC=N absorption. In the IR spectra of the complexes, this band is shifted to the region at 1605–1590 cm^{-1}, indicating coordination of the Schiff bases through the azomethine nitrogen.[9] A strong band at 1275–1260 cm^{-1} in the free Schiff bases has been assigned to the phenolic C-O absorption. On complexation this band is shifted to higher frequency, 1320–1290 cm^{-1}, indicating that coordination of the Schiff bases is through the phenolic oxygen atom.[10] This has been further supported by the disappearance of the broad ν(OH) band at 2950–2920 cm^{-1} in the complexes indicating deprotonation prior to coordination. The spectra of all the complexes show a very strong absorption at 1950 cm^{-1} due to the coordinated carbonyl group.[11] In the spectra of the complexes containing a coordinated nitrogen base, a medium-intensity band is observed in the 1020–1000 cm^{-1} region, which is characteristic of coordinated pyridine, piperidine or morpholine.[12] All the other characteristic absorptions due to triphenylphosphine have been observed in the expected regions.

Electronic Spectra

All the ruthenium(II) complexes are diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The ground state of ruthenium(II) (t_{2g}^6 configuration) in an octahedral environment is $^1A_{1g}$ and the excited states corresponding to the $t_{2g}^5\ e_g^1$ configuration are $^3T_{1g}$, $^3T_{2g}$, $^1T_{1g}$ and $^1T_{2g}$. 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 order of increasing energy. The electronic spectra of all these complexes in dichloromethane showed one or two bands in the 410–290 nm region (Table II). The bands in

Table II. IR (cm^{-1}) and Electronic Spectral (nm) Data of Ruthenium(II) Complexes

Complex	ν(C≡O)	ν(C-O)	ν(C=N)	λ_{max}	(∈)	Assignment
[Ru(CO)(*o*-hyacen)(PPh_3)]	1960 vs	1320 s	1590 vs	410	(727)	$^1A_{1g}\rightarrow{}^1T_{1g}$
				325	(2110)	charge transfer
[Ru(CO)(*o*-hyacen)(py)]	1945 vs	1290 s	1595 vs	400	(754)	$^1A_{1g}\rightarrow{}^1T_{1g}$
				325	(2009)	charge transfer
[Ru(CO)(*o*-hyacen)(pip)]	1960 vs	1300 s	1605 vs	415	(877)	$^1A_{1g}\rightarrow{}^1T_{1g}$
				295	(2341)	charge transfer
[Ru(CO)(*o*-hyacen)(morph)]	1950 vs	1295 s	1595 vs	410	(858)	$^1A_{1g}\rightarrow{}^1T_{1g}$
				300	(2089)	charge transfer
[Ru(CO)(*o*-hyacpn)(PPh_3)]	1940 vs	1300 s	1600 vs	390	(717)	$^1A_{1g}\rightarrow{}^1T_{1g}$
				305	(2234)	charge transfer
[Ru(CO)(*o*-hyacpn)(py)]	1940 vs	1300 s	1590 vs	400	(767)	$^1A_{1g}\rightarrow{}^1T_{1g}$
				320	(2038)	charge transfer
[Ru(CO)(*o*-hyacpn)(pip)]	1950 vs	1290 s	1595 vs	410	(879)	$^1A_{1g}\rightarrow{}^1T_{1g}$
				315	(2415)	charge transfer
[Ru(CO)(*o*-hyacpn)(morph)]	1950 vs	1295 s	1595 vs	410	(927)	$^1A_{1g}\rightarrow{}^1T_{1g}$
				310	(2312)	charge transfer
[Ru(CO)(*o*-hyactn)(PPh_3)]	1955 vs	1290 s	1600 vs	400	(757)	$^1A_{1g}\rightarrow{}^1T_{1g}$

				310	(2011)	charge transfer
[Ru(CO)(*o*-hyactn)(py)]	1945 vs	1290 s	1595 vs	400	(677)	$^1A_{1g} \rightarrow {}^1T_{1g}$
				315	(2067)	charge transfer
[Ru(CO)(*o*-hyactn)(pip)]	1950 vs	1295 s	1590 vs	410	(797)	$^1A_{1g} \rightarrow {}^1T_{1g}$
				290	(2567)	charge transfer
[Ru(CO)(*o*-hyactn)(morph)]	1955 vs	1300 s	1595 vs	400	(757)	$^1A_{1g} \rightarrow {}^1T_{1g}$
				295	(2987)	charge transfer
[Ru(CO)(*o*-hyac*o*pn)(PPh_3)]	1950 vs	1290 s	1600 vs	395	(827)	$^1A_{1g} \rightarrow {}^1T_{1g}$
				295	(2576)	charge transfer
[Ru(CO)(*o*-hyac*o*pn)(py)]	1960 vs	1300 s	1590 vs	390	(847)	$^1A_{1g} \rightarrow {}^1T_{1g}$
				295	(2867)	chargetransfer
[Ru(CO)(*o*-hyac*o*pn)(pip)]	1950 vs	1295 s	1595 vs	410	(751)	$^1A_{1g} \rightarrow {}^1T_{1g}$
				300	(2978)	chargetransfer
[Ru(CO)(*o*-hyac*o*pn)(morph)]	1950 vs	1290 s	1600 vs	400	(767)	$^1A_{1g} \rightarrow {}^1T_{1g}$
				305	(2987)	charge transfer

s = strong; vs = very strong; $\in$ in $dm^3\ mol^{-1}\ cm^{-1}$ units.

the 410–395 nm range have been assigned to the spin-allowed $^1A_{1g} \rightarrow ^1T_{1g}$ transition[13,14] based on the low extinction coefficient values ($\in$) as compared to charge transfer bands. The other high-intensity bands in the 325–290 nm region were assigned to charge transfer transitions.[15] The nature of the electronic spectra of all the complexes indicate an octahedral geometry around the ruthenium ion in the complexes and the spectra are very similar to the ones observed for other ruthenium(II) complexes.

^1H and ^{31}P NMR Spectra

The ^1H NMR spectra of the complexes were recorded to confirm the presence of the coordinated Schiff bases in the ruthenium(II) complexes. In the spectra of the complexes (Table III), a singlet was found at δ

Table III. ^1H and ^{31}P NMR Spectral Data of Ruthenium(II) Complexes

Complex	^1H NMR (ppm)	^{31}P NMR (ppm)
[Ru(CO)(*o*-hyacen)(PPh$_3$)]	1.62 (s, 6H, CH$_3$) 2.53–2.77 (t, 4H, 2CH$_2$, J = 8.6 Hz) 7.10–7.96 (m, aromatic)	a
[Ru(CO)(*o*-hyacen)(py)]	1.60 (s, 6H, CH$_3$) 2.50–2.80 (t, 4H, 2CH$_2$, J = 8.8 Hz) 7.10–8.00 (m, aromatic)	no signal
[Ru(CO)(*o*-hyacen)(pip)]	1.65 (s, 6H, CH$_3$) 2.65–2.77 (t, 4H, 2CH$_2$) 7.00–7.82 (m, 30H, aromatic)	a
[Ru(CO)(*o*-hyactn)(PPh3)]	1.68 (s, 6H, CH$_3$) 2.17–2.64 (m, 8H, 4CH$_2$) 7.00–7.90 (m, 30H, aromatic)	23.40
[Ru(CO)(*o*-hyactn)(py)]	1.70 (s, 6H, CH$_3$) 2.35–2.65 (m, 8H, 4CH$_2$) 7.00–7.80 (m, aromatic)	a
[Ru(CO)(*o*-hyactn)(pip)]	1.66 (s, 6H, CH$_3$) 2.20–2.52 (m, 8H, 4CH$_2$) 7.00–7.90 (m, aromatic)	a

a = not recorded.

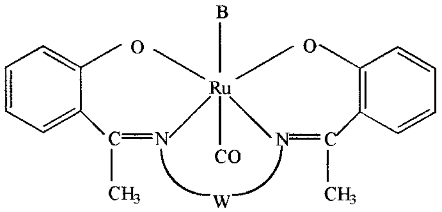
1.60–1.70 ppm corresponding to the methyl protons.[16] The methine proton signals were obtained in the region δ 2.17–2.80 ppm as a triplet for the first set of three complexes and as a multiplet for the second set of three complexes. A multiplet was observed around δ 7.00–8.00 ppm due to aromatic protons.

The ^{31}P NMR spectra were recorded for a few samples to confirm the presence of the triphenylphosphine group or heterocyclic nitrogen base in the complexes (Table III). The signal appearing at δ 23.40 ppm in the spectrum of (**9**) confirmed the presence of the triphenylphosphine group.[17] However, compound (**2**) exhibited no such signal confirming the absence of the triphenylphosphine group. This observation indicates the retention of coordinated pyridine or piperidine or morpholine in the complexes even after the coordination of the tetradentate Schiff bases. From the ^{31}P NMR spectra, it has been inferred that the Ru–P bond is more labile compared to the Ru–N bond in these complexes which is a reflection of the better σ-donating ability of the nitrogen bases compared to that of phosphorus in triphenylphosphine.

The following octahedral structure (Fig. 2) has been tentatively proposed for all of the new ruthenium(II) carbonyl complexes based on the analytical and spectral (IR, electronic, ^{1}H and ^{31}P NMR) data.

Antibacterial Activity Studies

The antibacterial activities of the complexes were studied by the Agar well-diffusion method.[18] Seven day old cultures of *E. coli* were used as a test organisms which were grown on a nutrient agar (NA) medium. Solutions of 1% , 2% and 4% of the complexes in DMSO were used for the studies. Antibacterial activity of one of the starting materials, namely $[RuHCl(CO)(PPh_3)_2(pip)]$, has been studied and it has been found that it did not exhibit activity against *E. coli*. Similar observation has been made earlier for $[RuH_2(CO)(PPh_3)_3]$ which showed activity higher than that of Schiff bases but lower than that of chelated complexes.[19] The results (Table IV) show that the ruthenium(II) carbonyl complexes have higher toxicity against the bacterial species than the free ligands. This can be attributed to Tweedy's chelation theory,[20] according to which the chelation reduces the polarity of the metal atom mainly because of the partial sharing of its positive charge with the group and possible π-electron delocalisation over the whole ring. This increases the lipophilic character of the metal chelate which favours its permeation through the lipid layers of bacterial membranes. Furthermore, the mode of action of the compounds may involve the hydrogen bond through the >C=N group with active centres of cell constituents resulting



Complex No.	B	W
(1)	PPh_3	$-(CH_2)_2-$
(2)	Py	$-(CH_2)_2-$
(3)	Pip	$-(CH_2)_2-$
(4)	Morph	$-(CH_2)_2-$
(5)	PPh_3	$-(CH(CH_3)CH_2)-$
(6)	Py	$-(CH(CH_3)CH_2)-$
(7)	Pip	$-(CH(CH_3)CH_2)-$
(8)	Morph	$-(CH(CH_3)CH_2)-$
(9)	PPh_3	$-(CH_2)_4-$
(10)	Py	$-(CH_2)_4-$
(11)	Pip	$-(CH_2)_4-$
(12)	Morph	$-(CH_2)_4-$
(13)	PPh_3	-*o*-(C_6H_4)-
(14)	Py	-*o*-(C_6H_4)-
(15)	Pip	-*o*-(C_6H_4)-
(16)	Morph	-*o*-(C_6H_4)-

Figure 2. Structure of the Ru(II) complexes.

Table IV. Antibacterial Activity Data of Ruthenium(II) Complexes

Compound	Diameter of Inhibition Zone (mm)		
	E. coil		
	1%	2%	4%
Co-Trimoxazole (standard antibiotic)	10	13	16
H_2(*o*-hyacen)	−2	−4	+1
[Ru(CO)(*o*-hyacen)(pip)]	+2	+3	+5
[Ru(CO)(*o*-hyacen)(morph)]	+5	+8	+10
H_2(*o*-hyacpn)	+1	+3	+6
[Ru(CO)(*o*-hyacpn)(pip)]	+4	+6	+10
[Ru(CO)(*o*-hyacpn)(morph)]	+7	+9	+14
H_2(*o*-hyac*o*pn)	+5	+8	+9
[Ru(CO)(*o*-hyac*o*pn)(py)]	+7	+11	+13
[Ru(CO)(*o*-hyac*o*pn)(morph)]	+9	+14	+17

1%, 2% and 4% indicate 1 g, 2 g and 4 g of the compound in 100 mL of test solution.

in the interference with normal cell process.[21] The activity of these complexes were compared with the complexes prepared using salicylaldehyde Schiff bases. The *o*-hydroxyacetophenone Schiff base complexes showed higher activity because of the presence of more electron donating groups (-CH_3) present in these complexes.[17] Also, the activity of the complexes reported here is higher compared with the standard antibiotic Co-Trimoxazole. The variation in the effectiveness of various compounds against various organisms depends either on the impermeability of the cells of the microbes or differences in ribosomes of microbial cells.[12] The inhibition activity of the new compounds increases with increase in the concentration of the solution.

CONCLUSION

The new ruthenium(II) complexes of the type [Ru(CO)(B)(L)] ($B = PPh_3$, pyridine, piperidine or morpholine; L = dianionic tetradentate Schiff bases) have been synthesised and characterised. An octahedral structure has been tentatively proposed for all the new complexes. The ligands, starting complex and new complexes have been subjected to antibacterial activity studies and it has been observed that chelation enhances the activity of the compounds.

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