含 NS 和 NNSS 供电子原子的钌(Ⅲ)席夫碱配合物：催化性能和抗微生物活性

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摘要：通过[$RuX_3(EPh_3)_3$] 或 [$RuBr_3(PPh_3)_2(MeOH)$] (式中 X=Cl 或 Br；E=P 或 As)与适当的席夫碱以 1:1 的物质的量的比反应合成了[$RuX_2(L')(EPh_3)_2$]或[$RuX(LL')(PPh_3)$](式中 L′=席夫碱配体 **1**，即[*S*-benzyl-*β*-*N*-(methyl,acetyl)methylenedithiocarbazate]; LL′=席夫碱配体 **6**，即 [Bis(*S*-benzyl-*β*-*N*-(methyl)methylenedithiocarbazate])2 种类型的钌(Ⅲ)配合物。席夫碱配体 **1** 和 **6** 分别由 *S*-benzyldithiocarbazate($NH_2NHCSSCH_2C_6H_5$)与 2,3-butanedione 以 1:1 and 1:2 的物质的量的比缩合反应而制得。用元素分析、光谱分析(IR、UV-Vis 和 EPR)和循环伏安法等对合成的席夫碱配合物进行了表征。结果表明合成的 Ru(Ⅲ)配合物显顺磁性。初步建议所有的新合成的配合物均为八面体结构。用乙醛与 H_2O_2 作为探针反应对合成的 Ru(Ⅲ)配合物的催化活性进行了评价。用 4 种细菌对席夫碱配体和由它们合成的 Ru(Ⅲ)配合物的抗微生物活性进行了筛选。

关键词：钌(Ⅲ)配合物；羰基氧；顺磁性；黏土催化剂；硫

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Catalytic and Antimicrobial Studies of Ruthenium(Ⅲ) Schiff Base Complexes Containing NS and NNSS Donor Atoms

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Abstract: Ruthenium(Ⅲ) complexes of the type [$RuX_2(L')(EPh_3)_2$] and [$RuX(LL')(EPh_3)$] (where, X=Cl or Br; E=P or As; L′-Schiff base ligand **1** [*S*-benzyl-*β*-*N*-(methyl,acetyl)methylenedithiocarbazate], LL′-Schiff base ligand **6** [Bis(*S*-benzyl-*β*-*N*-(methyl)methylenedithiocarbazate]) has been synthesized by the reactions of [$RuX_3(EPh_3)_3$] or [$RuBr_3(PPh_3)_2(MeOH)$] with appropriate Schiff bases in 1:1 molar ratio. The Schiff base ligands (**1** and **6**) were prepared by condensing *S*-benzyldithiocarbazate ($NH_2NHCSSCH_2C_6H_5$) with 2,3-butanedione (1:1 and 1:2 molar ratio). Complexes have been characterized by analytical, spectroscopic (IR, UV-Visible, and EPR) and Cyclic voltammetric methods. The ruthenium(Ⅲ) complexes are paramagnetic and an octahedral structure has been tentatively proposed for all the new complexes. Catalytic activity of these complexes has been explored by means of a probe reaction of the acetaldehyde with H_2O_2. The ligands and the complexes were screened for antimicrobial activity against four organisms.

Key words: ruthenium(Ⅲ); keto oxygen; paramagnetic; clay catalyst; sulphur

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In recent years there has been a great deal of interest in synthesis and characterization of transition metal complexes containing Schiff base as ligands, due to their importance as catalyst for many reactions [1]. Furthermore, Schiff base complexes are important for designing metal complexes related to synthetic and natural oxygen carriers[2]. One interest in the study of compounds containing sulphur and nitrogen arises from their significant antifungal, antibacterial and anticancer activity, also the nitrogen-sulphur donor ligands have been of great interest to researchers [3]. *S*-alkyl and *S*-benzyl derivatives of dithiocarbazate has been synthesized and investigated over the past few decades [4~12]. Dithiocarbazic acid and the Schiff bases derived from its *S*-alkyl and *S*-benzyl esters form an interesting series of ligands. Researchers in this area have synthesized new nitrogen-sulphur donor ligands through Schiff base condensation with various aldehydes and ketones. The properties of these ligands can be greatly modified by introducing organic substituents. The number of this type of compound synthesised continues to increase because of the intriguing observation that different ligands show different biological properties, although they may differ only slightly in their molecular structures [13~17]. Transition metal complexes of these ligands are also widely studied because of their potential for therapeutic use [18], in health and skin care products and in paint manufacturing[19].

During the course of our systematic investigation on the reactions of dithiocarbazic acid and the Schiff bases derived from its *S*-alkyl and *S*-benzyl esters and related ligands with ruthenium(Ⅲ) complexes, we intended to study the catalytic activity of the complexes towards the oxidation of alcohol and the effect of extra sulphur atom present in the ligand on antimicrobial studies. With a view to obtaining the coordination behavior of NS and NNSS chromophores in bi- and tridentate Schiff bases, we report in the present paper the synthesis, characterization, electrochemistry, catalytic and antimicrobial activities of ruthenium(Ⅲ) complexes.

1 Experimental

IR spectra were recorded using KBr pellets in the 4000~400 cm^{-1} region on a Nexus FTIR spectrophotometer. Elemental analyses (C,H,N and S) were carried out by using Carlo Erba 1 106 analyser. Metal determination were carried out using a Perkin-Elmer Plasma 1 000 Emission spectrometer. ^{1}H-NMR spectra were recorded on a Brucker 400 MHz spectrometer. The UV-Visible spectra were recorded in CH_2Cl_2 on Hitachi-Elmer Model 20/200 spectrophotometer in the range of 800~200 nm. EPR spectra of powder samples at room temperature were recorded with model ER 200-D Bruker spectrometer at X-band frequencies. Magnetic susceptibilities were recorded on an G-PARC vibrating sample magnetometer. Cyclic voltammetric studies were carried out with a BAS CV-27 voltammeter in acetonitrile using a glassy-carbon electrode as working electrode and the potentials were referenced to saturated calomel electrode. Melting points were recorded on Micro heating table and are uncorrected.

All the reagents used were of A.R. grade. Solvents were purified and dried according to standard procedures [20]. $RuCl_3 \cdot 3H_2O$ was purchased from Sigma-Aldrich and used without further purification. The starting complexes, $[RuCl_3(PPh_3)_3]$, $[RuCl_3(AsPh_3)_3]$, $[RuBr_3(AsPh_3)_3]$ and $[RuBr_3(PPh_3)_2(MeOH)]$ and ligands (**1** [*S*-benzyl-*β*-*N*-(methyl,acetyl)methylenedithiocarbazate] and **6** [Bis(*S*-benzyl-*β*-*N*-(methyl)methylenedithiocarbazate]) were prepared by literature methods[21,22].

1.1 Preparartion of $[RuX_2(L')(EPh_3)_2]$ (2~5) (X= Cl or Br; L′=NS Schiff base ligand 1; E=P or As)

All the preparations were carried out under strictly anhydrous conditions. The Schiff bases (0.021~0.029 g; 0.01 mmol) were added to a benzene solution of $[RuX_3(EPh_3)_3]$ or $[RuBr_3(PPh_3)_2(MeOH)]$ (0.090~0.125 g; 0.01 mmol) in 1∶1 molar ratio and the mixtures were refluxed for 5 h. The dark green solutions obtained were concentrated to about 5 mL. The complexes were precipitated by the addition of small quantity of petroleum ether (60~80 ℃). The complexes were then filtered, washed with petroleum ether and recrystallized from CH_2Cl_2/petroleum ether (60~80 ℃) and dried under vacuum. Its purity was checked by TLC (Aluminium sheets 20×20 cm: silica gel 60 F_{254};

eluant: Petroleum ether/Chloroform: 3/1; R_f:0.53). Yield: 86%~90%.

1.2 Prepararion of [RuX(LL′)(EPh_3)] (7~10)(X= Cl or Br; LL′=Schiff base ligand 6; E=P or As)

All the preparations were carried out under strictly anhydrous conditions. The Schiff bases (0.035~0.050 g; 0.01 mmol) were added to a benzene solution of [$RuX_3(EPh_3)_3$] or [$RuBr_3(PPh_3)_2$(MeOH)] (0.090~0.125 g; 0.01 mmol) in 1:1 molar ratio and the mixtures were refluxed for 5 h. The dark green solutions obtained were concentrated to about 5 mL. The complexes were precipitated by the addition of small quantity of petroleum ether (60~80 ℃). The complexes were then filtered, washed with petroleum ether and recrystallized from CH_2Cl_2/ petroleum ether (60~80 ℃) and dried under vacuum. Its purity was checked by TLC (Aluminium sheets 20×20 cm: silica gel 60 F_{254}; eluant: Petroleum ether/Chloroform: 3/1; R_f:0.54). Yield: 85%~88%.

1.3 Catalytic studies

The catalytic reaction was carried out in a 50 mL three-neck flask fitted a reflux condensor. An aqueous solution of H_2O_2 (10 mL; 0.10 mol) was pipetted out and added into an aqueous solution of CH_3CHO (5.70 mL; 0.05 mol). The resulting solution was heated to 60 ℃, then powdered complex samples were added to this solution. The mixture was heated for 3 h at the same temperature and the reaction was monitored by TLC at regular intervals. The reaction was stopped after confirmed the formation of ethanoic acid and the catalyst was separated by the filtration. A standard NaOH solution was used to titrate the reactant solution. The formation rate of the ethanoic acid produced [$mmol \cdot (g\ catalyst)^{-1} \cdot h^{-1}$] was taken in order to assess the catalytic activity.

1.4 Qualitative antimicrobial assay

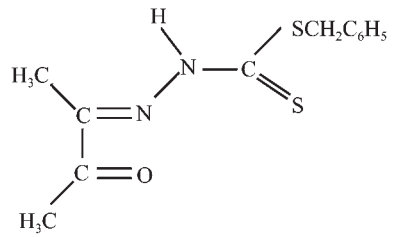
Four pathogenic microbials were used to test the antibacterial activity of the Schiff bases and its metal complexes. They were (Ⅰ) Salmonella aureus, (Ⅱ) Salmonella typhi, (Ⅲ) Eenterobacteria feacalis and (Ⅳ) Aeromonas hydrophilla. Antimicrobial activity of the extracts was qualitatively determined by a disc diffusion method[23]. The bacteria were cultured in nutrient agar medium and used for the study. Bacterial cells were swabbed on to nutrient agar medium in Petri plates. The compounds to be tested were dissolved in DMSO and soaked in filter paper discs (Whatmann No. 4 of 6 mm diameter). These discs were placed on the already seeded plates and incubated at 26±1 ℃ for 24 h. The zones of inhibition around the discs were measured after 24 h. Streptomycin and Colistin were used as positive controls.

2 Results and Discussion

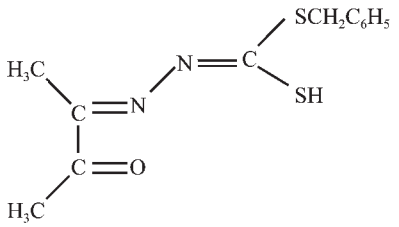
2.1 [$RuX_2(L')(EPh_3)_2$] (2~5); [RuX(LL′)(EPh_3)] (7~10) (X=Cl or Br; L′=Schiff base 1; LL′= Schiff base 6; E=P or As)

Physico-chemical data and yield for this compounds are given in Table 1. This Schiff base can exhibit thione and thiol tautomerism, since it has a thioamide function, -NH-C(=S)$SCH_2C_6H_5$.

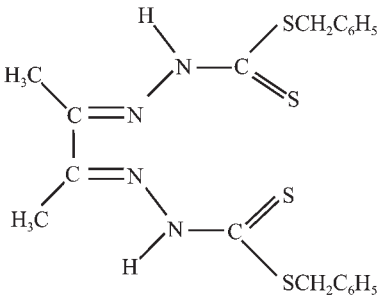
IR and UV-Visible spectral data of the ligands and ruthenium(Ⅲ) complexes are given in Table 2. The IR spectrum of the ligands (**1** and **6**) does not exhibit any ν(S-H) band at ca. 2 700 cm^{-1}, but displays the ν(N-H) band at ca. 3 230 and 3 170 cm^{-1}, respectively, indicating that, in the solid state, it remains as the thione form (**1**a and **6**a). ^{1}H-NMR spectrum does not show any peaks at ca. δ 4.0 ppm attributable to S-H proton, suggesting that the thiol forms are absent, even in solution. However, in solution, in the presence of ruthenium ion, it quickly changes to the thiol forms (**1**b and **6**b) with concomitant formation of the ruthenium(Ⅲ) complexes of the deprotonated thiolate form of the ligands. The azomethine ν(C=N) bands of the ligands (NS and NNSS type) around 1 610 and 1 620 cm^{-1}, respectively, shift to lower region in the spectra of all the complexes (Table 2), showing the coordination of the azomethine nitrogens to the metal [24]. The absence of ν(N-H) at 3 230 and 3 170 cm^{-1} and ν(C=S) at 1 030 and 1 070 cm^{-1} in the IR spectrum of the metal complexes, suggests that these ligands lose one and two protons upon complexation, thus acting as a uninegative bidentate ligand (NS) and binegative quadridentate ligand (NNSS), respectively. The ν(C=O) band of



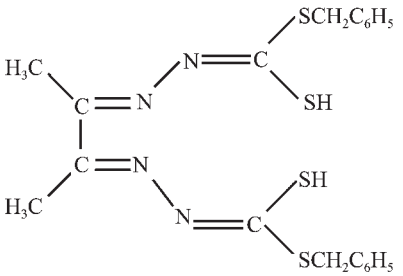
(**1**a) (thione form)



(**1**b) (thiol form)



(**6**a) (thione form)



(**6**b) (thiol form)

Table 1 Physico-chemical data of ligands and ruthenium(Ⅲ) complexes

Complex	Colour	M.P. / ℃	Yield	Analysis:Found (cacld.) / %				μ_{eff} / B.M.
				C	H	N	S	
($C_{12}H_{14}ON_2S_2$)(**1**)	Yellow	134.9	90	54.56(54.11)	5.64(5.30)	10.79(10.52)	24.10(24.05)	—
[$RuCl_2$($C_{12}H_{13}ON_2S_2$)(PPh_3)$_2$](**2**)	Green	174.4	87	59.88(59.92)	4.78(4.51)	2.58(2.91)	6.70(6.66)	1.88
[$RuCl_2$($C_{12}H_{13}ON_2S_2$)($AsPh_3$)$_2$](**3**)	Green	167.2	88	54.73(54.90)	4.20(4.13)	2.60(2.67)	6.05(6.10)	1.88
[$RuBr_2$($C_{12}H_{13}ON_2S_2$)($AsPh_3$)$_2$](**4**)	Green	173.2	86	50.30(50.61)	3.70(3.81)	2.74(2.46)	5.81(5.62)	1.92
[$RuBr_2$($C_{12}H_{13}ON_2S_2$)(PPh_3)$_2$](**5**)	Green	162.9	90	54.80(54.85)	4.50(4.13)	2.80(2.67)	6.12(6.09)	1.90
($C_{20}H_{22}N_4S_4$)(**6**)	Yellow	220.1	94	53.29(53.79)	4.90(4.97)	12.61(12.55)	28.89(28.69)	—
[RuCl($C_{20}H_{20}N_4S_4$)(PPh_3)](**7**)	Green	161.7	88	62.76(62.22)	4.47(4.81)	7.48(7.64)	17.30(17.47)	1.93
[RuCl($C_{20}H_{20}N_4S_4$)($AsPh_3$)](**8**)	Green	153.4	85	51.26(51.43)	4.02(3.98)	6.50(6.32)	14.45(14.43)	1.90
[RuBr($C_{20}H_{20}N_4S_4$)($AsPh_3$)](**9**)	Green	162.5	85	48.70(48.97)	3.87(3.79)	6.42(6.01)	13.90(13.75)	1.92
[RuBr($C_{20}H_{20}N_4S_4$)(PPh_3)](**10**)	Green	183.0	87	51.21(51.40)	4.08(3.98)	6.56(6.31)	14.50(14.43)	1.90

Table 2 IR and Electronic spectral data of ligands and ruthenium(III) complexes

Complex	ν(C=O) / cm^{-1}	ν(C=N) / cm^{-1}	ν(N-H) / cm^{-1}	ν(C=S) / cm^{-1}	ν(Ru-Cl/Br) / cm^{-1}	λ_{max} / nm
1	1676 s	1610 vs	3231 s	1030 s	-	—
2	1672 s	1595 vs	—	—	321	550,321
3	1674 s	1590 vs	—	—	320	540,322
4	1674 s	1595 vs	—	—	319	545,325
5	1675 s	1590 vs	—	—	320	530,330
6	—	1620 vs	3170 s	1070 s	—	—
7	—	1600 vs	—	—	320	559, 308
8	—	1600 vs		—	320	549,302
9	—	1595 vs	—	—	320	555,323
10	—	1600 vs	—	—	555, 323	535,312

s:strong; vs:very strong

the Schiff base (NS) remains unaffected indicating that coordination does not occur through the keto oxygen. This is further supported by the absence of ν(Ru-O) in the spectrum of complexes suggesting that the keto oxygen does not participate in coordination. For all the complexes, ν(Ru-Cl/Br) absorption has been observed around ~320 cm^{-1}. All the other characteristic bands due to triphenylphosphine/arsine and ligands were also presented in the expected region. It is therefore apparent that the Schiff bases coordinate in a uninegatively (**1**) and binegatively (**6**) charged rather than an ONS tridentate manner.

The electronic spectra of all the complexes (Table 2) in dichloromethane showed two bands in the 550~321 (**2~5**) and 559~302 nm (**7~10**) region. The bands around 550~530 and 559~535 nm region, respectively, have been assigned to $^2T_{2g} \rightarrow {}^2T_{1g}$ transitions. The other high intensity bands in the 321~330 and 323~302 nm region have been assigned charge transfer bands on the basis of high extinction coefficient value (ε=10 450~17 590 and 12 450~18 590 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$). The nature of the electronic spectra of all the complexes indicate an octahedral geometry around ruthenium ion in the complexes and the spectra are very similar to the ones observed for other ruthenium(Ⅲ) complexes [25]. All the ruthenium(Ⅲ) complexes are paramagnetic, indicating the presence of ruthenium in the +3 oxidation state.

The magnetic moment values obtained lie in the 1.88 to 1.92 B.M. (**2~5**) and 1.90 to 1.93 B.M. (**7~10**) range, corresponds to one unpaired electron, suggesting a low spin t^5_{2g} confugration for the ruthenium(Ⅲ) ion in octahedral environment.

The redox potentials of the complexes are characterized by well-defined waves in the 0.43 to 0.66 V range (oxidation) and −0.57 to −0.67 V (reduction) (**2~5**) and 0.58 to 0.65 V range (oxidation) and −0.56 to −0.64 V (reduction) (**7~10**) versus a saturated calomel electrode (SCE). The electrochemical data are given in Table 3. All the complexes showed a reversible redox ($Ru^{Ⅳ}$-$Ru^{Ⅲ}$ and $Ru^{Ⅲ}$-$Ru^{Ⅱ}$) wave with a peak to peak separation (E_P) ranging from 60~100 mV and from 80~100 mV, respectively, indicating a single step one-electron transfer process. Fast electron transfers are expected for low-spin six-coordinate ruthenium(Ⅲ) complexes, since electron can be added to or removed from t_{2g} orbitals. These orbitals are sterically more accessible than the e_g orbitals, and electron changes within the t_{2g} set require less reorganisation energy than changes within e_g orbitals. There appears to be little variation in the redox potentials due to the substitution of triphenylphosphine by triphenylarsine in the complexes. Hence, it has been observed from the electrochemical data, that the present ligand system is ideally suited for stabilizing the +3 oxidation state of the ruthenium[21].

Table 3　Cyclic voltammetric data[a] of ruthenium(III) complexes

Complex	Ru(Ⅳ)-Ru(Ⅲ)				Ru(Ⅲ)-Ru(Ⅱ)			
	E_{pc} / V	E_{pa} / V	E_f / V	ΔE_p / mV	E_{pa} / V	E_{pc} / V	E_f / V	ΔE_p / mV
2	0.66	0.58	0.62	80	−0.52	−0.62	−0.57	100
3	0.46	0.39	0.43	70	−0.65	−0.59	−0.62	60
4	0.56	0.63	0.60	70	−0.63	−0.70	−0.67	70
5	0.70	0.62	0.66	80	−0.58	−0.67	−0.63	90
7	0.69	0.60	0.65	90	−0.52	−0.60	−0.56	80
8	0.68	0.60	0.64	80	−0.60	−0.68	−0.64	80
9	0.67	0.58	0.64	90	−0.66	−0.58	−0.62	80
10	0.63	0.53	0.58	100	−0.53	−0.61	−0.57	80

[a]Supporting electrolyte: $[NBu_4]ClO_4$ (0.05 $mol \cdot L^{-1}$); Concentration of the complexes: 0.01 $mol \cdot L^{-1}$; Scan rate: 50 $mV \cdot s^{-1}$; all the potentials are referred to silver-silver chloride electrode; E_f=0.5 (E_{pa}+E_{pc}) where, E_{pa} and E_{pc} are the aniodic and cathodic potentials, respectively.

EPR spectra of the complexes exhibit a $g_\perp$ value at ca. 2.20~2.36 and $g_{//}$ at ca. 2.09~2.17 (**2~5**) and ca. 2.20~2.30 and ca. 2.10~2.17 (**7~10**), respectively, (Table 4). The two different g values (g_x=g_y≠g_z) indi-

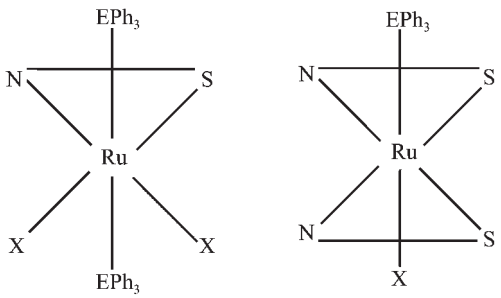
cate a tetragonal distortion in octahedral complexes[24]. The presence of two *g* values also indicates an axial symmetry for these complexes. Though a structure with *cis*-Cl/Br and PPh_3/$AsPh_3$ ligands is possible for new complexes, we tentatively assigned a trans structure, because it will have less strain in accommodating the tetradentate ligand around the ruthenium ion[26].

Table 4 EPR spectral data[a] of ruthenium(Ⅲ) complexes

Complex	g_x	g_y	g_z	<g>*
2	2.36	2.36	2.17	2.30
3	2.24	2.24	2.09	2.26
4	2.27	2.27	2.15.	2.23
5	2.20	2.20	2.12	2.17
7	2.30	2.30	2.17	2.26
8	2.27	2.27	2.15	2.23
9	2.24	2.24	2.10	2.19
10	2.20	2.20	2.12	2.17

[a] $<g>^* = \sqrt{(g_x^2+g_y^2+g_z^2)/3}$

Based on the analytical, spectroscopic data (IR, UV-Visible and EPR) and electrochemical data, an octahedral structure as shown in the following figures has been proposed for all ruthenium(Ⅲ)) complexes.



(a) (b)

(E=P or As; X=Cl or Br)

Structures of ruthenium(Ⅲ) Schiff base complexes

(a) **2~5** and (b) **7~10**.

2.2 Catalytic activity

In order to investigate the oxidative catalytic activity of the complexes (**3**) and (**7**), we carried out the oxidation of acetaldehyde by H_2O_2 using complexes (**3**) and (**7**) as the catalysts. Under the same experimental conditions, complexes (**3**) and (**7**) has the catalytic activity of 72.0 and 72.1 mmol ethanoic acid/g catalyst/h, respectively, while Ni_2Al-CO_3, i.e. the clay catalyst $Ni_{0.70}Al_{0.30}(OH)_2 \cdot 0.15CO_3 \cdot 0.86H_2O$, has an activity of 8.0 [27]. The catalytic activity shows an increase of around 9 times for complexes (**3**) and (**7**) over Ni_2Al-CO_3. In the absence of the complexes, there is no change in the formation rate of the ethanoic acid indicating the catalytic activity of the new complexes. The catalytic selectivity for ethanoic acid was nearly 100%. This suggests that these ruthenium(Ⅲ) complexes may become a highly active oxidation catalyst in organic synthesis.

2.3 Quantitative antimicrobial assay

The *in vitro* antibacterial screening of the ligands and their ruthenium(Ⅲ) complexes have been tested and the results are shown in Table 5. Among the complexes and ligands tested, the ligand. (H_2-NNSS Schiff base) and their appropriate complexes have been found to be more toxic against all the four species of bacteria than the other ligand (NS Schiff base) and its appropriate complexes under similar conditions. The increased activity of these compounds may be possibly due to the presence of extra sulphur atoms[28,29]. It has been observed from the antibacterial screening studies that the ruthenium chelates have higher activity than the corresponding free ligands against the same microorganism under identical experimental conditions, which is consistent with earlier reports[30]. The possible mode of increased activity of the ruthenium complexes compared to that of the free ligands may be due to the chelation, it reduces the polarity of the central ion mainly because of the partial sharing of its positive charge with the donor groups and possible π-electron delocalisation within the whole chelate ring. This chelation increases the liophilic nature of the central atom which favours its permeation through lipid layers of the cell membrane[31~33]. Furthermore, the mode of action of the compounds may involve the hydrogen bond through >C=N group with active centers of cell constituents resulting in the interference with normal cell process [34]. Though the complexes possess activity, it could not reach the effectiveness of the standard drugs. Few compounds were inactive against different organisms, the variation in the effectiveness of different compounds against different organisms depends either on the imperme-

Table 5　Antibacterial activity data of ligands and ruthenium(III) complexes

Compound	Diameter of inhibition zone / mm			
	S. aureus	*S. typhi*	*E. feacalis*	*A. hydrophilla*
Streptomycin sulphate	18	16	19	22
Colistin	17	23	16	20
1	9	8	7	10
2	11	10	11	13
3	11	—	11	14
4	10	10	12	12
5	13	12	11	13
6	11	10	10	11
7	13	14	14	–
8	14	14	12	13
9	14	13	13	–

ability of the cells of the microbes or differences in ribosomes of microbial cells[35].

3　Acknowledgement

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