含 NS 和 NNSS 供电子原子的钌(Ⅱ)羰基配合物

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摘要：通过[RuHCl(CO)(PPh_3)$_2$(B)] (B=PPh_3, 吡啶 (py), 哌啶 (pip), 吗啉 (morph))与适当的席夫碱按 1:1 的物质的量的比反应，合成了二齿和四齿席夫碱钌(Ⅱ)配合物。所用席夫碱配体通过 *S*-苄基二硫代肼基甲酸酯与 2,3-丁二酮(物质的量的比分别为 1:1 和 1:2)的缩合反应制得。通过元素分析和多种物理化学方法对钌(Ⅱ)配合物和其席夫碱配体进行了表征。钌(Ⅱ)配合物为六配位的反磁性物质。用三种细菌对席夫碱配体及其钌(Ⅱ)配合物的抗微生物活性进行了筛选试验。

关键词：钌(Ⅱ); 羰基配合物；席夫碱；供电子体
中图分类号：O614.82$^+$1 **文献标识码**：A **文章编号**：1001-4861(2006)06-1055-07

Ruthenium(Ⅱ) Carbonyl Complexes Containing NS and NNSS Donor Atoms

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Abstract: Bidentate and tetradentate Schiff base ruthenium(Ⅱ) complexes has been synthesized by the reaction of [RuHCl(CO)(PPh_3)$_2$(B)] (B=PPh_3 or pyridine (py) or piperidine (pip) or morpholine (morph)) with appropriate Schiff bases in 1:1 molar ratio. The Schiff base ligands were prepared by condensing *S*-benzyldithiocarbazate ($NH_2NHCSSCH_2C_6H_5$) with 2,3-butanedione (1:1 and 1:2 molar ratio). Ruthenium(Ⅱ) complexes and the ligands were studied and characterized by elemental analyses and various physico-chemical methods. The ruthenium complexes were diamagnetic with six-coordinate structures. The ligands and the complexes were screened for antimicrobial activity against three organisms.

Key words: ruthenium(Ⅱ); carbonyl complexes; Schiff base; donor atom

Dithiocarbazate, NH_2NHCS_2, and its *S*-alkyl and *S*-benzyl derivatives have been synthesized and investigated over the past few decades[1~9]. An interesting series of Schiff base ligands has been derived from dithiocarbazic acid and its *S*-alkyl and *S*-benzyl esters. Researchers in this area have synthesized new nitrogen-sulphur donor ligands through Schiff base condensation with various aldehydes and ketones. Also the nitrogen-sulphur donor ligands have been of great interest to researchers. The properties and characters of these ligands can be greatly modified by introduction of organic substituents. Although they may differ only slightly in their molecular structures, the number of this type of compounds synthesized continues to increase because of the intriguing observation that different ligands show different biological proper-

收稿日期：2006-02-02。收修改稿日期：2006-04-27。
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ties[10~14]. Transition metal complexes of these ligands are also widely studied because of their potential for therapeutic use [15]. They also find applications in health and skin care products and in paint manufacturing[16].

During the course of our systematic investigations on the reactions of S-benzyl dithiocarbazate and related ligands with transition metal complexes, we intended to study 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 tetra-dentate Schiff bases, we report here the synthesis, characterization, spectral and antimicrobial activities of ruthenium(Ⅱ) complexes.

1 Experimental

All reagents used were of AnalaR grade. Solvents were purified and dried according to standard procedures[17]. $RuCl_3 \cdot 3H_2O$ was purchased and used without further purification. The starting complexes [18,19] and ligands[20] were prepared by reported literature methods.

IR spectra were recorded in KBr pellets, in the 4 000~400 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 was carried out using a Perkin-Elmer Plasma 1 000 Emission spectrometer. ^1H NMR and ^{31}P NMR spectra were recorded on a Brucker 400 MHz instrument using TMS and o-phosphoric acid as an internal reference, respectively. Electronic spectra were recorded in CH_2Cl_2 on Hitachi-Elmer Model 20/200 spectrophotometer in the range 800 ~200 nm. Magnetic susceptibilities were measured with a Johnson Matthey magnetic susceptibility balance at 298 K. All the susceptibilities were corrected for the diamagnetic contribution using Pascal′s constant. Melting points were recorded on Micro heating table and were uncorrected.

1.1 Preparation of uninegative bidentate Schiff base ligand (1)

S-benzyl-*β*-*N*-(methyl,acetyl)methylenedithiocarbazate (NS Schiff base) ($C_{12}H_{14}ON_2S_2$)

S-benzyldithiocarbazate ($NH_2NHCSSCH_2C_6H_5$) (4.95 g; 0.025 mol) was dissolved in absolute ethanol (25 mL). To this solution 2,3-butanedione (1.65 g; 0.025 mol) also in absolute ethanol (20 mL) was added. The mixture was heated with stirring for 20 min and then allowed to stand for 15 min, whereupon a yellow precipitate formed. It was filtered off, washed with ethanol and dried in vacuum over P_2O_5. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (98/2, V/V) as eluant. The purity of the compounds was checked by TLC (Aluminium sheets 20×20 cm: silica gel 60 F_{254}; eluant: ethanol; R_f: 0.52).

1.2 Preparation of [RuCl(CO)(L′)(PPh_3)(B)](2~5)

(L′=NS Schiff base; B=PPh_3 or pyridine (py) or piperidine(pip) or morpholine(morph)

All the preparations were carried out under strictly anhydrous conditions. The Schiff bases (0.027~0.034 g; 0.01 mmol) were added to a benzene solution of [RuHCl(CO)(PPh_3)$_2$(B)] (B=PPh_3 or py or pip or morph) (0.077~0.095 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. The purity was checked by TLC. Yield : 85%~90%

1.3 Preparation of binegative tetradentate Schiff base ligand(6)

Bis (*S*-benzyl-*β*-*N*-(methyl)methylenedithiocarbazate (NNSS Schiff base) ($C_{20}H_{22}N_4S_4$)

S-benzyldithiocarbazate ($NH_2NHCSSCH_2C_6H_5$) (9.90 g; 0.050 mol) was dissolved in absolute ethanol (25 mL). To this solution 2,3-butanedione (1.65 g; 0.025 mol) also in absolute ethanol (20 mL) was added. The mixture was heated with stirring for 20 min and then allowed to stand for 15 min, whereupon a yellow precipitate formed. It was filtered off, washed with ethanol and dried in vacuum over P_2O_5. The crude product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (97/3,

V/*V*) as eluant. The purity of the compounds was checked by TLC (Aluminium sheets 20 × 20 cm: silica gel 60 F_{254}; eluant: ethanol; R_f: 0.54).

1.4 Preparation of [Ru(CO)(LL′)(B)] (7~10)

(LL′=NNSS Schiff base; B=PPh_3 or py or pip or morph)

All the preparations were carried out under strictly anhydrous conditions. The Schiff bases (0.046~0.058 g; 0.01 mmol) were added to a benzene solution of $[RuHCl(CO)(PPh_3)_2(B)]$ (B=PPh_3 or py or pip or morph) (0.077~0.095 g; 0.01 mmol) in 1:1 molar ratio and the mixtures were refluxed for 5 h. The dark green colored 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. The purity was checked by TLC. Yield: 87%~90%

1.5 Preparation of antimicrobial assay medium

Three pathogenic microbials were used to test the biological potential of the Schiff bases and its metal complexes. They were (i) *Bacillus sp*., (ii) *E.Coli* and (iii) *Pseudomonas sp*. Antimicrobial activity of the extracts was qualitatively determined by a disc diffusion method [21]. The bacteria were cultured in nutrient agar medium and used for the study. Bacterial cells were swabbed onto nutrient agar medium in Petri plates. The compounds to be tested were dissolved in DMF and soaked in filter paper discs (Whatmann No.4 of 5 mm diameter). These discs were placed on the already seeded plates and incubated at 25 ± 1 ℃ for 36 h. The zones of inhibition around the discs were measured after 36 h. Streptomycin and Colistin were used as positive controls.

2 Results and Discussion

2.1 [RuCl(CO)(L′)(PPh_3)(B)] (2~5); [Ru(CO)(LL′)(B)] (7~10)

(L′=NS Schiff base; LL′=NNSS Schiff base; B=PPh_3 or py or pip or morph)

Physico-chemical data and yield of Schiff bases and complexes are given in Table 1. These Schiff bases can exhibit thione and thiol tautomerisms, since both has a thioamide function, -NH-C(=S)$SCH_2C_6H_5$.

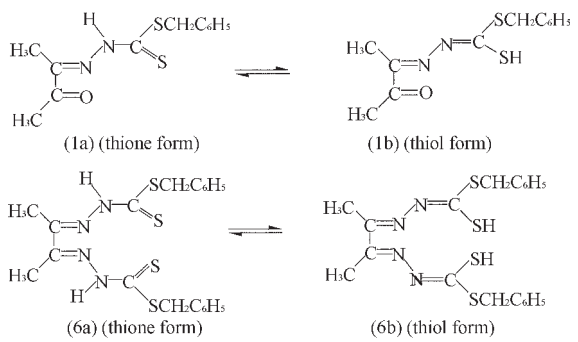


Table 1　Analytical data of ligands and ruthenium(Ⅱ) complexes

Complex	Colour	m.p. / ℃	Found (calcd.) /%			
			C	H	N	S
($C_{12}H_{14}ON_2S_2$) (**1**)	Yellow	134.9	54.56(54.11)	5.40(5.30)	10.49(10.52)	24.10(24.05)
[RuCl(CO)($C_{12}H_{13}ON_2S_2$)(PPh_3)$_2$] (**2**)	Green	154.4	61.88(61.65)	4.85(4.54)	2.88(2.94)	6.70(6.71)
[RuCl(CO)($C_{12}H_{13}ON_2S_2$)(PPh_3)(py)] (**3**)	Green	166.2	56.03(56.05)	4.30(4.32)	5.60(5.45)	8.35(8.30)
[RuCl(CO)($C_{12}H_{13}ON_2S_2$)(PPh_3)(pip)] (**4**)	Green	178.2	55.30(55.68)	4.90(4.94)	5.74(5.41)	8.21(8.25)
[RuCl(CO)($C_{12}H_{13}ON_2S_2$)(PPh_3)(morph)] (**5**)	Green	161.9	54.10(53.93)	4.80(4.79)	5.50(5.39)	8.12(8.22)
($C_{20}H_{22}N_4S_4$) (**6**)	Yellow	220.1	53.29(53.79)	4.90(4.97)	12.61(12.55)	28.89(28.69)
[Ru(CO)($C_{20}H_{20}N_4S_4$)(PPh_3)] (**7**)	Green	151.7	56.76(56.03)	4.27(4.22)	6.48(6.70)	15.30(15.32)
[Ru(CO)($C_{20}H_{20}N_4S_4$)(py)] (**8**)	Green	159.4	45.56(45.66)	4.02(3.69)	10.50(10.24)	18.45(18.73)
[Ru(CO)($C_{20}H_{20}N_4S_4$)(pip)] (**9**)	Green	161.5	45.70(45.33)	4.37(4.39)	10.42(10.17)	18.90(18.60)
[Ru(CO)($C_{20}H_{20}N_4S_4$)(morph)] (**10**)	Green	183.0	43.21(43.40)	4.28(4.23)	10.56(10.13)	18.50(18.52)

IR, UV-Visible and NMR spectral data of ligands and ruthenium(Ⅱ) 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 (1a and 6a). ^{1}HNMR 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 (1b and 6b) with concomitant formation of the ruthenium(Ⅱ) 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, shifted to lower region in the spectra of all the complexes, showing the coordination of the azomethine nitrogens to the metal [22]. 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 proton upon complexation, thus acting as a uninegative bidentate ligand (NS) and binegative quadridentate ligand (NNSS), respectively. The ν(C=O) band of 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 (**2~5**), suggesting that the keto oxygen does not participate in coordination. The spectra of all the complexes (**2~5** and **7~10**) show a very strong absorption at ca. 1 950 cm^{-1} due to the coordinated terminal carbonyl group[23]. In the complexes containing a coordinated nitrogen base, a medium intensity band is observed in the 1 000~1 020 cm^{-1} region characteristic of the coordinated pyridine, piperidine and morpholine[24]. For all

Table 2 IR, UV-Visible and NMR spectral data of ligands and ruthenium(Ⅱ) complexes

Complex	$\nu_{(C=O)}$ / cm^{-1}	$\nu_{(C-O)}$ / cm^{-1}	$\nu_{(C=N)}$ / cm^{-1}	$\nu_{(N-H)}$ / cm^{-1}	$\nu_{(C=S)}$ / cm^{-1}	λ_{max} / nm	^{1}H NMR (δ / ppm)	^{31}P NMR (δ / ppm)
1	—	1 676	1 610	3 231	1 030	—	—	a
2	1 950	1 673	1 590	—	—	550,350	1.70(s, 6H, $2CH_3$), 3.83(s, 2H, CH_2), 7.10~7.90(m, aromatic)	26.54
3	1 952	1 675	1 590	—	—	520,382	1.60(s, 6H, $2CH_3$), 3.92(s, 2H, CH_2), 7.11~7.98(m, aromatic)	26.53,43.50
4	1 984	1 675	1 595		—	480,375	1.64(s, 6H, $2CH_3$), 4.00(s, 2H, CH_2), 7.20~8.00(m, aromatic)	a
5	1 949	1 674	1 595	—	—	502,330	1.67(s, 6H, $2CH_3$), 3.80(s, 2H, CH_2), 7.20~8.00(m, aromatic)	a
6	—	—	1 620	3 170	1 070	—	—	a
7	1 955	—	1 605	—	—	560,388	1.63(s, 6H, $2CH_3$), 3.85(s, 4H, $2CH_2$), 7.20~8.00(m, aromatic)	26.74
8	1 960	—	1 600	—	—	537,392	1.61(s, 6H, $2CH_3$), 3.83(s, 4H, $2CH_2$), 7.22~8.00(m, aromatic)	a
9	1 955	—	1 595		—	512,375	1.73(s, 6H, $2CH_3$), 3.98(s, 4H, $2CH_2$), 7.20~8.00(m, aromatic)	No signal
10	1 950	—	1 600	—	—	520,400	1.67(s, 6H, $2CH_3$), 3.91(s, 4H, $2CH_2$), 7.20~8.00(m, aromatic)	a

s-singlet; m-multiplet; a-not recorded

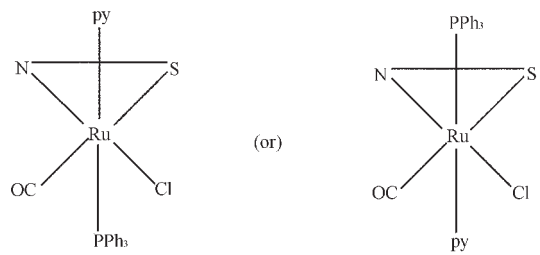
the complexes, ν(Ru-Cl) absorption has been observed around ~320 cm^{-1}. All the other characteristic bands due to triphenylphosphine and ligands were also presented in the expected region.

All the ruthenium(Ⅱ) complexes are diamagnetic, indicating the presence of ruthenium in the +2 oxidation state. The electronic spectra of all the complexes in dichloromethane show two bands in the 550~330 (for complexes **2~5**) and 560~375 nm (for complexes **7~10**) region. The bands in the 550~480 and 560~512 nm region have been assigned to the spin-allowed $^1A_{1g} \rightarrow {}^1T_{1g}$ transitions, respectively. The other high intensity bands in the 382~330 and 400~375 nm region have been assigned to charge transfer bands on the basis of high extinction coefficient value (ε=9 450~11 590 and 8 580~9 950 $dm^3 \cdot mol^{-1} \cdot cm^{-1}$, respectively). 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(Ⅱ) complexes[25].

The ^{1}H NMR spectra of the complexes were recorded to confirm the presence of coordinated Schiff bases in the ruthenium(Ⅱ) complexes. In the spectra of the complexes (**2~5** and **7~10**), a sharp singlet was found in the δ 1.60~1.70 and 1.61~1.73 ppm corresponding to the methyl protons, respectively. The methylene protons at ca. δ 3.80~4.00 and 3.80~4.00 ppm occur as a singlet and a multiplet at *ca.* δ 7.10~8.00 and 7.10~8.00 ppm due to the aromatic protons, respectively.

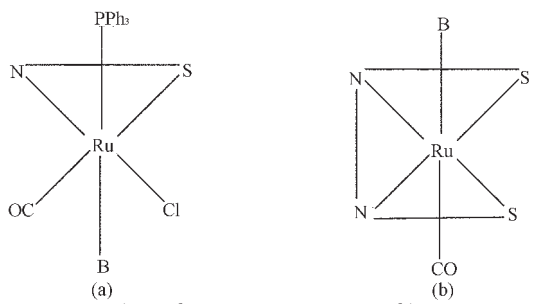
^{31}P NMR spectra of two complexes [RuCl(CO)($C_{12}H_{13}ON_2S_2$)(PPh_3)$_2$] (**2**) and [RuCl(CO)($C_{12}H_{13}ON_2S_2$)(PPh_3)(py)] (**3**) were recorded in order to ascertain whether or not the PPh_3 or the heterocyclic base has been substituting during the course of the reaction. In the spectra of (**2**), the appearance of one singlet at ca. δ 26.54 ppm revealed the presence of magnetically equivalent phosphorus atoms, suggesting that the two PPh_3 groups are trans to each other in the complex. The spectrum of (**3**) showed two singlets at *ca.* δ 26.53 and δ 43.50 ppm in the intensity ratio of 2:1. This observation leads to two possible structures arising from the mixture of two isomers, the intensity of the peaks depending upon the percentage of the isomers present[26].

The two possible isomers are,



^{31}P NMR spectra of two complexes [Ru(CO)($C_{20}H_{20}N_4S_4$)(PPh_3)] (**7**) and [Ru(CO)($C_{20}H_{20}N_4S_4$)(pip)] (**9**) were recorded. A singlet at *ca.* δ 26.74 ppm in the spectrum of (**7**), confirm the presence of triphenylphosphine. However, (**9**) exhibits no such signal confirming the absence of triphenylphosphine in the complex. This observation reveals the presence of coordinated pyridine or piperidine or morpholine in the complexes even after the coordination of tetradentate Schiff base.

Attempts to crystallize the ligand complexes in different solvents failed. In general, reactions of the ligands (NS and NNSS Schiff base) with starting metal complexes were quick and gave good yields of mononuclear complexes corresponding to the general formula [RuCl(CO)(L′)(PPh_3)(B)] and [Ru(CO)(LL′)(B)] (L′=NS Schiff base; LL′=NNSS Schiff base; B=PPh_3 or py or pip or morph), respectively. The new complexes are air- and light- stable and soluble in most of the common organic solvents. Molecular weight determination (Rast method) and elemental analyses data confirm the complexes to be hexa-coordinated.



(B=PPh_3 or py or pip or morph)

Structures of ruthenium(Ⅱ) carbonyl Schiff base complexes (a) **2~5** and (b) **7~10**.

2.2 Antimicrobial studies

The *in vitro* antibacterial screening of the ligands and their ruthenium(Ⅲ) complexes have been tested and the results are showed in Table 3. Among the complexes and ligands tested, the ligand (H_2-NNSS Schiff base) and its appropriate complexes have been found to be more toxic against all the three 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[27,28]. 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[29]. The possible mode of increased activity of the ruthenium complexes compared to that of the free ligands may be due to the chelation which 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 lipophilic nature of the central atom which favours its permeation through lipid layers of the cell membrane[30~33]. 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 impermeability of the cells of the microbes or differences in ribosomes of microbial cells[35].

Table 3 Antibacterial activity data of ligands and ruthenium(Ⅲ) complexes

Compound	Diameter of inhibition zone / mm		
	Bacillus sp.	E.Coli	Pseudomonas sp.
Streptomycin sulfate	8	8	9
Colistin	9	8	9
1	3	1	4
2	5	4	5
3	5	4	6
4	4	—	5
5	3	5	6
6	3	3	5
7	6	6	—
8	7	6	7
9	6	7	8
10	7	6	7

3 Acknowledgement

We gratefully acknowledge the financial support from the Brain Korea 21 Project and National Research Laboratory for Environmental Catalysis.

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