



Transition metal salts dependent intramolecular cyclization of a diimine

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ARTICLE INFO

Article history:

Received 1 September 2009

Received in revised form 1 October 2009

Accepted 13 October 2009

Available online 10 November 2009

Keywords:

Transition metal

Imidazole

Intramolecular cyclization

Diimine

ABSTRACT

1,4-Bis(N-tosylethylamino)-2,3-diphenyl-1,4-diaza-1,3-butadiene (L^1) was separated from a condensation reaction of benzil with N-tosyl-ethylenediamine. It was shown that the intramolecular cyclization of L^1 has much dependence on the transition metal salts. The transformation of L^1 in the absence of any transition metal salts gave product 1-tosylaminoethyl-2-tosylaminomethyl-4,5-diphenyl-1H-imidazole (L^2) at a temperature above 100 °C. Similar reactions assisted by $Ni(CH_3COO)_2 \cdot 4H_2O$, $MnCl_2 \cdot 4H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$ or $NiSO_4 \cdot 7H_2O$ could also give L^2 at a much lower temperature and a much higher yield. However, the presence of $Cu(CH_3COO)_2 \cdot H_2O$ in a similar transformation reaction led to the formation of a bicyclic derivative 1-tosyl-5,6-diphenyl-1H-2,3-dihydroimidazo[1,2-a]imidazole (L^3). But both L^2 and L^3 were not detected when $Co(CH_3COO)_2 \cdot 4H_2O$ was used in a similar reaction and all attempts to transform L^2 into L^3 failed.

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1. Introduction

The synthesis of imidazole and its derivatives presents much interests in recent years due to their wide applications in biochemical processes [1,2], catalysis [3–7], electron transport systems [8] and nanoparticle electrosynthesis [9–11]. This might be partly ascribed to the application of a large class of imidazoles as ionic liquid and the imidazoles related N-heterocyclic carbenes [1,12]. There are numerous methods reported in literatures for the synthesis of imidazoles [12]. In summary, they can be divided into two types: intermolecular cyclization from multi-components and intramolecular cyclization from one component. The synthesis of imidazole ring via intermolecular cyclization from multi-components have been extensively studied, such as the reaction of diimine with a CH_2 donor [3,13–15] and the four component condensation of aryl glyoxals, primary amines, carboxylic acids and isocyanides on wang resin [16]. However, the intramolecular cyclization to form imidazole ring from one component was much less studied [17–19]. And only one was reported to form imidazole ring from diimine via intramolecular cyclization catalyzed by transition metal salts [19]. In recent years, the use of transition metal complexes as catalysts has received considerable interest in different areas of organic transformations to afford the product in excellent yields owing to the advantages such as inexpensive non-toxic and eco-friendly nature. Based on this fact, we intend to introduce transition metal salts to mediate the synthesis of imidazole ring via intramolecular cyclization. Therefore we report here the synthesis of a diimine from the reaction of benzil with N-tosyl-ethylenedia-

mine and the studies on the effect of transition metal salts on the formation imidazole ring and its bicyclic derivative from the diimine.

2. Results and discussion

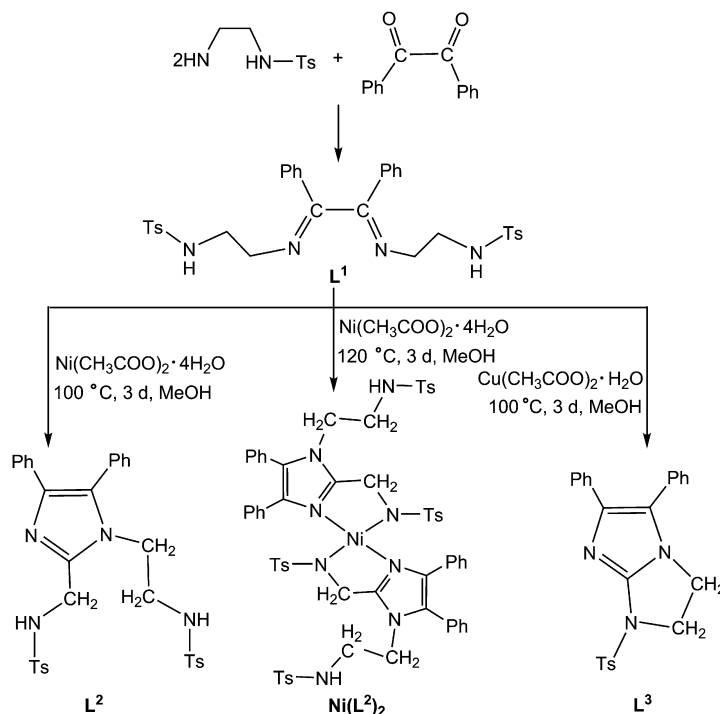
2.1. Synthesis of L^1 , L^2 , $Ni(L^2)_2$ and L^3

The synthesis of L^1 and the transition metal salts mediated transformation of L^1 into L^2 and L^3 are described in Scheme 1. N-Tosyl-ethylenediamine was synthesized from the reaction of ethylenediamine with 4-toluene sulfonyl chloride according to a literature method [20,21]. The reaction of N-tosyl-ethylenediamine with benzil in ethanol at 90 °C gave L^1 in a yield of 70% after recrystallization from ethanol. Attempts to carry out this reaction at lower temperature (60 °C and 80 °C) failed to obtain the product of L^1 . The 1H NMR spectrum of compound L^1 shows two multiplet signals at 3.35–3.26 and 3.25–3.20 ppm for the four CH_2 groups and a singlet at 2.43 ppm for the two chemically identical CH_3 groups. The ^{13}C NMR spectrum of compound L^1 reveals also two signals at 52.8 and 43.7 ppm for the four CH_2 groups and a singlet at 21.4 ppm for the two chemically identical CH_3 groups. The NMR information reveals the formation of compound L^1 .

The transformation of L^1 in the presence of $Ni(CH_3COO)_2 \cdot 4H_2O$ in a solvothermal reaction was carried out in methanol at 100 °C for 3 days, giving L^2 in a yield of 72%. Similar reactions using $MnCl_2 \cdot 4H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$ or $NiSO_4 \cdot 7H_2O$ instead of $Ni(CH_3COO)_2 \cdot 4H_2O$ gave also L^2 as shown in Table 1. It is noteworthy that no product was identified when the reaction in the presence of $Mn(CH_3COO)_2 \cdot 4H_2O$ was carried out at or below

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**Table 1**

Transformation of **L**¹ into **L**² or **L**³ mediated by different transition metal salts in hydrothermal reactions with a molar ratio of transition metal salt: **L**¹ = 1:1 under 100 °C for 3 days.

	Transition metal salt	Solvent	Product	Yield (%)
1	Ni(CH ₃ COO) ₂ ·4H ₂ O	Methanol	L ²	72
2	Ni(CH ₃ COO) ₂ ·4H ₂ O	Ethanol	L ²	68
3	NiCl ₂ ·6H ₂ O	Methanol	L ²	58
4	Ni SO ₄ ·7 H ₂ O	Methanol	L ²	70
5	Mn(CH ₃ COO) ₂ ·4H ₂ O	Methanol	L ²	68
6	Mn(CH ₃ COO) ₂ ·4H ₂ O	Ethanol	L ²	64
7	MnCl ₂ ·4H ₂ O	Methanol	L ²	50
8	Cu(CH ₃ COO) ₂ ·H ₂ O	Methanol	L ³	60

80 °C. Furthermore, it was found that the presence of Ni(CH₃COO)₂·4H₂O in the solvothermal transformation reaction for 3 days led to part transformation of **L**¹ into **L**² at 60 °C and overall transformation of **L**¹ into **L**² above 80 °C. However, using NiCl₂·6H₂O instead of Ni(CH₃COO)₂·4H₂O, the solvothermal transformation reaction with a duration of 3 days gave no **L**² at 60 °C, but induced an overall transformation of **L**¹ into **L**² above 80 °C. In contrast, the similar reaction was also carried out in the absence of any transition metal salts. It gave also product **L**², but only at a temperature above 100 °C and in a much lower yield. All of these facts seem to

suggest that different transition metal salts have some contribution on the transformation of **L**¹ into **L**².

To confirm further the contribution of transition metal salts on the transformation of **L**¹ into **L**², the reactions in the absence or presence of Ni(CH₃COO)₂·4H₂O with different ratios of Ni(CH₃COO)₂·4H₂O to **L**¹ were monitored at different temperatures by TLC techniques in routine solution reactions, as shown in Table 2. It was shown that no product was identified when the reaction mixture in the absence of Ni(CH₃COO)₂·4H₂O was kept at or below the temperature of 80 °C. The attempted transformation of **L**¹ into **L**² at 50 °C in the presence of Ni(CH₃COO)₂·4H₂O with a 1:1 ratio of Ni(CH₃COO)₂·4H₂O to **L**¹ failed also to afford any product. However the transformation of **L**¹ into **L**² in the presence of Ni(CH₃COO)₂·4H₂O with a 1:1 ratio of Ni(CH₃COO)₂·4H₂O to **L**¹ is completed within 2 h at 60 °C and 1.5 h at 80 °C. When the ratios of Ni(CH₃COO)₂·4H₂O to **L**¹ were changed into 1:2 and 1:10, the similar transformation reactions at 80 °C were completed within 3.5 and 9 h, respectively, as shown in Table 2. All of these confirm that Ni(CH₃COO)₂·4H₂O have some contribution in the transformation of **L**¹ into **L**². The transformation of **L**¹ into **L**² mediated by Ni(CH₃COO)₂·4H₂O was also tried by solvothermal reactions in a 25 mL Teflon-lined autoclave. The difference from the corresponding routine solution reaction mentioned above is that the solvothermal reaction at 50 °C gave also a very small amount of product **L**².

Table 2

Investigation on the transformation of **L**¹ into **L**² assisted by Ni(CH₃COO)₂·4H₂O in routine solution reactions at different temperatures monitored by TLC technique.

	Catalyst	Catalyst:substrate	Solvent	T (°C)	Time (h)	Product
1	Ni(CH ₃ COO) ₂ ·4H ₂ O	0.1 mmol:0.1 mmol	Methanol	50	10	No reaction
2	No transition metal salt		Methanol	50	10	No reaction
3	Ni(CH ₃ COO) ₂ ·4H ₂ O	0.1 mmol:0.1 mmol	Methanol	60	2	L ²
4	No transition metal salt		Methanol	60	10	No reaction
5	Ni(CH ₃ COO) ₂ ·4H ₂ O	0.1 mmol:0.1 mmol	Ethanol	80	1.5	L ²
6	No transition metal salt		Ethanol	80	10	No reaction
7	Ni(CH ₃ COO) ₂ ·4H ₂ O	0.1 mmol:0.2 mmol	Ethanol	80	3.5	L ²
8	Ni(CH ₃ COO) ₂ ·4H ₂ O	0.1 mmol:1 mmol	Ethanol	80	9	L ²

However the solvothermal reaction at 120 °C gave a complex of L^2 , $Ni(L^2)_2$, not just L^2 .

The solvent effect on the formation of L^2 was investigated by the use of dichloromethane, ethanol, methanol and H_2O as solvents in the transformation reactions of L^1 into L^2 in the presence of $Ni(CH_3COO)_2 \cdot 4H_2O$ in a sealed 25 mL Teflon-lined autoclave at 60 °C. It was shown that only methanol and ethanol can serve as the solvents in the reactions. The reactions using dichloromethane and water as solvents failed to give L^2 .

L^2 was identified by elemental analysis, infrared spectroscopy, mass spectroscopy, NMR and single crystal X-ray diffraction analysis. The existence of three chemically different CH_2 groups in compound L^2 are confirmed by one doublet at 4.35 ppm, one triplet at 3.94 ppm and one quadruplet at 2.85 ppm in the 1H NMR spectrum of L^2 and three signals at 44.2, 42.6 and 39.3 ppm in the ^{13}C NMR spectrum of compound L^2 . It is further shown that there are two chemically different CH_3 groups revealed by two singlet at 2.44 and 2.42 ppm in the 1H NMR spectrum of L^2 . All of the NMR information demonstrates the formation of compound L^2 from L^1 , consistent with the X-ray diffraction analysis result.

However, the solvothermal transformation of L^1 mediated by $Cu(CH_3COO)_2 \cdot H_2O$ instead of other transition metal salts mentioned above at 100 °C for 3 days produced a bicyclic derivative L^3 in a yield of 60%. L^3 was identified by elemental analysis, infrared spectroscopy, mass spectroscopy, NMR and single crystal X-ray diffraction analysis. Compound L^3 exhibits two triplets at 4.30 and 3.90 ppm in the 1H NMR spectrum and two signals at 51.6 and 41.4 ppm in the ^{13}C NMR spectrum for the two chemically different CH_2 groups and one singlet at 2.44 ppm in the 1H NMR spectrum and one signal at 21.7 ppm in the ^{13}C NMR spectrum for the only one CH_3 group. This is consistent with the structure of compound L^3 confirmed by the X-ray diffraction analysis.

But both L^2 and L^3 were not detected when $Co(CH_3COO)_2 \cdot 4H_2O$ was used in a similar reaction. All attempts to transform L^2 into L^3 in the presence of any transition metal salts mentioned above failed.

Proposed mechanisms for the transformation of L^1 into L^2 and L^3 are shown in Scheme 2. It reveals some similarities to those

reported by the group of Datta [19] and the group of Yaylayan [22]. In the case reported by Datta the binding of L (L = 1:2 condensate of benzil and 2-(aminomethyl)pyridine) to zinc seems to be a prerequisite for the formation of imidazole ring. However it seems to be not necessary for the formation of L^2 in our case because the formation of L^2 could also occur even with the absence of transition metal salts as revealed by the experimental facts. Nevertheless, the presence of transition metal salts makes it much easier for the formation of L^2 probably due to the much easier release of H^+ from L^1 upon its coordination to transition metal ions. For the formation of L^3 from L^1 the coordination of L^1 to Cu^{2+} seems to be a prerequisite as suggested by the experimental studies described above in the context. The tentative mechanism for the formation of L^3 is demonstrated by the experimental fact of failing to transform L^2 into L^3 . In the last step of the proposed mechanisms for the transformation of L^1 into L^2 and L^3 an aerial oxidation is implicated to complete the formation of the corresponding imidazole rings. To confirm the occurrence of aerial oxidation during the reaction course for the formation of both L^2 and L^3 , we carried out the solvothermal transformation reactions under N_2 atmosphere in the presence of $Ni(CH_3COO)_2 \cdot 4H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$, respec-

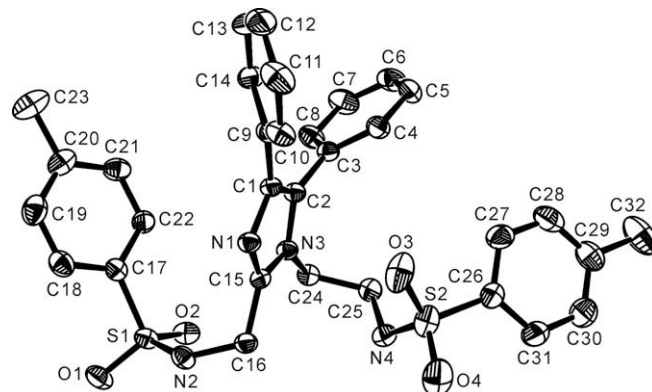
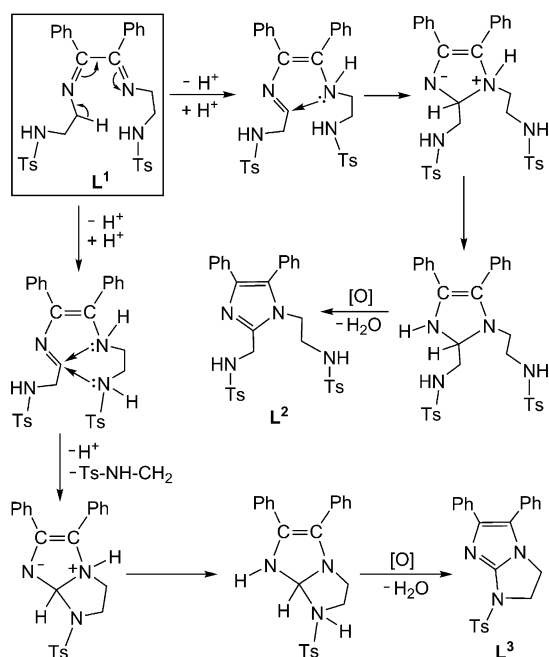


Fig. 1. ORTEP view of the structure of L^2 showing the atom-labeling scheme and 30% thermal ellipsoids.



Scheme 2. Proposed mechanisms for the transformation of L^1 into L^2 and L^3 . [O] = oxidation.

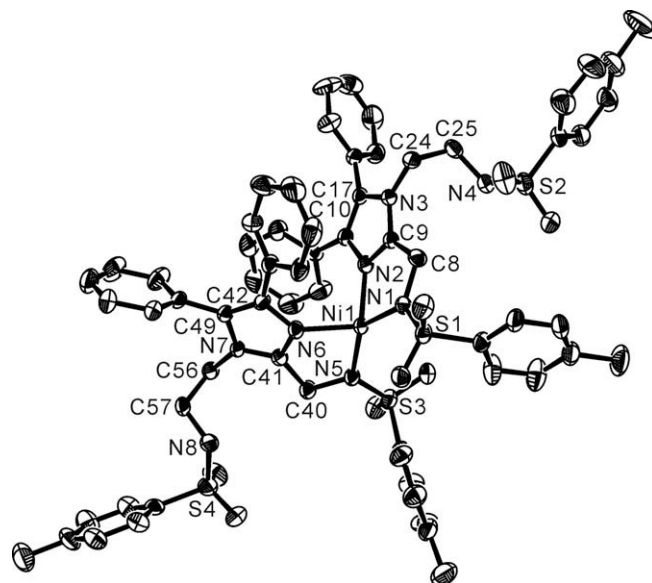


Fig. 2. ORTEP view of the structure of $Ni(L^2)_2$ showing the atom-labeling scheme and 30% thermal ellipsoids.

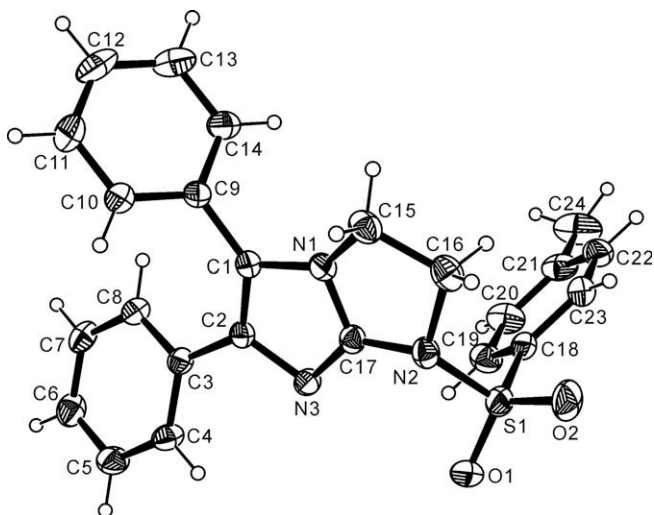


Fig. 3. ORTEP view of the structure of L^3 showing the atom-labeling scheme and 30% thermal ellipsoids.

tively. As expected, no product L^2 or L^3 was found in both cases due to the absence of oxygen.

2.2. Crystal structure studies of L^2 , $Ni(L^2)$ and L^3

An ORTEP view of the structure of L^2 is shown in Fig. 1. It is shown that N1, C1, C2, N3 and C15 are nearly located in one plane and the N1–C1, C1–C2, C2–N3, N3–C15 and C15–N1 bond lengths and the corresponding bond angles (Table 4) in the ring are comparable to those in the imidazole ring reported [23–26]. This confirms the existence of the imidazole ring in compound L^2 .

The crystal structure of $Ni(L^2)_2$ (Fig. 2) shows the chelation of L^2 to the Ni(II) ion using one imidazole ring nitrogen atom and one amino nitrogen atom. Each Ni(II) ion is four-coordinated by two $[L^2]^-$ ions to form a severely distorted tetrahedral geometry. The bond lengths and angles (Table 4) in the ring are comparable to the corresponding ones in L^2 .

The crystal structure of L^3 is shown in Fig. 3. It reveals the presence of an imidazole ring N1C1C2N3C17 in compound L^3 as demonstrated by the bond lengths and angles shown in Table 4. It demonstrates also the formation of another five-membered heterocyclic ring of N1C15C16N2C17.

3. Conclusion

In this research work, a diimine was separated from a condensation reaction of benzil with N-tosyl-ethylenediamine. The transition metal salts mediated intramolecular cyclization of the diimine was investigated. It was shown that the presence of $Ni(CH_3COO)_2 \cdot 4H_2O$, $MnCl_2 \cdot 4H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$ or $NiSO_4 \cdot 7H_2O$ could lead to the formation of a substituted imidazole with one imidazole ring at a much lower temperature and a much higher yield than the similar case in the absence of any transition metal salts. However, a similar transformation reaction in the presence of $Cu(CH_3COO)_2 \cdot H_2O$ gave a bicyclic derivative. But both products were not detected when $Co(CH_3COO)_2 \cdot 4H_2O$ was used in a similar reaction and all attempts to transform L^2 into L^3 failed.

4. Experimental

4.1. General procedures

All chemicals were used as obtained without further purification. Infrared spectra were recorded as KBr pellet using a Nicolet

360FT-IR spectrometer. Elemental analyses (C, H and N) were performed on a Vario EL analyzer. 1H and ^{13}C NMR spectra were recorded on a Bruker AV 500 spectrometer at 500.13 and 125.23 MHz, respectively. All proton and carbon chemical shifts are reported in δ units with reference to $SiMe_4$. Melting points were measured on an X-6 melting point apparatus and were uncorrected. Analytical TLC's were performed on pre-coated Merck silica gel 60 F254 plates; the spots were detected either under UV light or by placing in iodine chamber.

4.2. Synthesis of L^1

N-Tosyl-ethylenediamine (0.856 g, 4 mmol) was dissolved in 20 mL ethanol, which was stirred using a magnetic stirrer. Benzil (0.42 g, 2 mmol) dissolved in a 10 mL of ethanol was added dropwise using a dropping funnel to the above solution. The mixture was heated in an oil bath at $90^\circ C$, the completion of reaction was monitored by TLC. Twenty hours later, the solution was cooled to ambient temperature over a period of 6 h. The thus formed white-yellow crystalline product was collected by filtration, washed with ethanol twice (2×5 mL) and dried in vacuo. Finally the product was recrystallized from ethanol to give pure needle crystals (yield: 70%). m.p.: $159-161^\circ C$. Elemental analysis calcd (%) for $C_{32}H_{34}O_4N_4S_2$: C, 63.76; H, 5.69; N, 9.29. Found: C, 63.42; H, 5.92; N, 9.50. 1H NMR ($CDCl_3$, ppm): $\delta = 7.76$ (d, $J = 8.5$ Hz, 4H), 7.63 (d, $J = 7.5$ Hz, 4H), 7.46 (t, $J = 7.5$ Hz, 2H), 7.37 (t, $J = 8$ Hz, 4H), 7.29 (t, $J = 8.5$ Hz, $CH-C(CH_3)=CH$, 4H), 3.35–3.26 (m, $C=N-CH_2$, 4H), 3.25–3.20 (m, $S-N-CH_2$, 4H), 2.43 (s, CH_3 , 6H). ^{13}C NMR ($CDCl_3$, TMS): $\delta = 21.4$ (s, CH_3), 43.7 ($S-N-CH_2$), 52.8 ($C=N-CH_2$), 127.1, 127.2, 128.9, 129.6, 131.4, 135.0 ($N=C-C$), 143.3 (CH_3-C), 167.2 ($C=N$) ppm. IR (KBr, pellet)/ cm^{-1} : 3445m, 3153m, 2902w, 1626m, 1598m, 1578w, 1494w, 1449m, 1327s, 1305m, 1291m, 1252w, 1169s, 1108m, 1091m, 1073m, 1033w, 928m, 900w, 815m, 774m, 695m, 661m, 598w, 577m, 550m. MS[m/z]: 601.94. ($M-H^+$).

4.3. Synthesis of L^2

A mixture of nickel(II) acetate tetrahydrate (0.0248 g, 0.1 mmol), L^1 (0.0602 g, 0.1 mmol) and methanol (10 mL) was sealed in a 23 mL Teflon-lined autoclave and heated at $100^\circ C$ for 3 days. Then it was cooled over a period of 24 h and filtered. The evaporation of the filtrate at ambient temperature for 2 days gave colorless crystals of compound (L^2). Yield: 0.0433 g (72%). m.p.: $215-218^\circ C$. Elemental analysis calcd (%) for $C_{32}H_{32}O_4N_4S_2$: C, 63.98; H, 5.37; N, 9.33. Found: C, 63.54; H, 5.05; N, 9.65. 1H NMR ($CDCl_3$, ppm): 7.79 (d, $J = 8$ Hz, 2H), 7.68 (d, $J = 8$ Hz, 2H), 7.42 (t, $J = 7$ Hz, 1H), 7.36–7.30 (m, 6H), 7.17–7.04 (m, 5H), 6.93 (d, $J = 7$ Hz, 2H), 4.35 (d, $J = 5.5$ Hz, $-C-CH_2-NH-SO_2-$, 2H), 3.94 (t, $J = 6$ Hz, $-N-CH_2-CH_2-NH-SO_2-$, 2H), 2.85 (q, $^3J_{HH} = 6.0$ Hz, $^3J_{HH} = 6.5$ Hz, $CH_2-CH_2-NH-SO_2-$, 2H), 2.44 (s, CH_3 , 3H), 2.42 (s, CH_3 , 3H). ^{13}C NMR ($CDCl_3$, ppm): $\delta = 143.8$, 143.6, 143.0, 136.7, 136.4, 131.0, 129.9, 129.8, 129.4, 128.3, 127.1, 127.0, 126.6, 44.2, 42.6, 39.3, 21.5. IR (KBr, pellet)/ cm^{-1} : 3438s, 3262m, 1630m, 1598m, 1498w, 1426m, 1385m, 1342s, 1312m, 1165s, 1147s, 1122m, 1093s, 976w, 811m, 774m, 699m, 577w, 554m, 527w.

4.4. Synthesis of $Ni(L^2)_2$

Nickel(II) acetate tetrahydrate (0.0248 g, 0.1 mmol) was added into a methanol solution (10 mL) of L^1 (0.0602 g, 0.1 mmol). The resulted mixture was transferred into a 23 mL Teflon-lined autoclave, heated at $120^\circ C$ for 2 days. It was then cooled over a period of 10 h and filtered. The filtrate was allowed to evaporate at ambient temperature for 4 h, giving purple crystals of $Ni(L^2)_2$ in a yield of 85%. Elemental analysis calcd (%) for $C_{64}H_{62}N_8NiO_8S_4$:

C, 61.10; H, 4.97; N, 8.91. Found: C, 60.74; H, 5.31; N, 8.74. IR (KBr, pellet)/cm⁻¹: 3446m, 3186m, 3060w, 2925w, 1627w, 1600m, 1493s, 1441m, 1335s, 1269m, 1161vs, 1144vs, 1125s, 1103m, 1082m, 1053w, 1021w, 997m, 954m, 817m, 783m, 771m, 734m, 708m, 688s, 664s, 587m, 555s, 517w.

4.5. Synthesis of L³

A mixture of copper(II) acetate tetrahydrate (0.0200 g, 0.1 mmol), L¹ (0.0602 g, 0.1 mmol), and methanol (10 mL) was sealed in a 23 mL Teflon-lined autoclave and heated at 100 °C for 3 days. It was then cooled over a period of 10 h and filtered. The filtrate was allowed to evaporate at ambient temperature for 2 days, giving crystals of compound L³ in a yield of 60% (0.0349 g). Elemental analysis calcd (%) for C₂₄H₂₁N₃O₂S: C, 69.37; H, 5.09; N, 10.11. Found: C, 69.72; H, 5.42; N, 9.90. ¹H NMR (CDCl₃, ppm): δ = 8.03 (d, *J* = 7.5 Hz, 2H), 7.60 (d, *J* = 6 Hz, 2H), 7.36–7.19 (m, 10H), 4.30 (t, *J* = 7 Hz, Ph–C–N–CH₂, 2H), 3.90 (t, *J* = 7 Hz, Ts–N–CH₂, 2H), 2.44 (s, CH₃, 3H). ¹³C NMR (CDCl₃, TMS): δ = 145.0, 134.8, 133.5, 130.1, 129.8, 128.9, 128.5, 128.3, 128.1, 127.9, 127.4, 126.8, 51.6 (Ph–C–N–CH₂), 41.4 (s, Ts–N–CH₂), 21.7 (s, CH₃). IR (KBr pellet)/cm⁻¹: 3436s, 3059w, 2933w, 1603m, 1578w, 1546s, 1490m, 1449m, 1443m, 1369s, 1350m, 1299m, 1242w, 1186s, 1170vs, 1136m, 1091m, 1008m, 943w, 815m, 792m, 734m, 708s, 700s, 672s, 650m, 586s, 550m.

4.6. X-ray crystallography

The selected single crystals of L², Ni(L²)₂ and L³ were put in a sealed tube and the measurement was performed on a Bruker Smart Apex-II CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Absorption correction were ap-

Table 3
Crystal data and structure refinement parameters for compounds L², Ni(L²)₂ and L³.

	L ²	Ni(L ²) ₂	L ³
Formula	C ₃₂ H ₃₂ N ₄ O ₄ S ₂	C ₆₄ H ₆₂ N ₈ NiO ₈ S ₄	C ₂₄ H ₂₁ N ₃ O ₂ S
Fw	600.74	1258.17	415.50
<i>T</i> (K)	296(2)	296(2)	296(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	P $\bar{1}$	P $\bar{1}$	P2 ₁ /n
<i>a</i> (Å)	10.2330(16)	14.561(9)	12.6496(16)
<i>b</i> (Å)	10.8187(17)	15.519(13)	10.2211(13)
<i>c</i> (Å)	15.153(3)	16.677(14)	17.033(2)
α (°)	94.647(2)	64.053(10)	90
β (°)	101.098(2)	82.914(18)	106.417(2)
γ (°)	112.845(2)	71.91(3)	90
<i>V</i> (Å ³)	1494.4(4)	3221(4)	2112.4(5)
<i>Z</i>	2	2	4
<i>D</i> _c (g cm ⁻³)	1.335	1.297	1.306
μ (mm ⁻¹)	0.222	0.490	0.179
<i>F</i> (0 0 0)	632	1316	872
Crystal size (mm)	0.20 × 0.15 × 0.15	0.25 × 0.20 × 0.20	0.20 × 0.20 × 0.15
θ (°)	2.07–25.01	2.02–25.01	2.35–27.45
Reflections collected/unique	7792/5174	16,397/11,061	12,900/4799
<i>R</i> _{int}	0.0256	0.0255	0.0518
GOF on <i>F</i> ²	1.060	1.090	1.007
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>)) ^a	0.0522	0.0824	<i>R</i> ₁ = 0.0545
<i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>)) ^b	0.1154	0.2608	<i>wR</i> ₂ = 0.1051
<i>R</i> ₁ (all data) ^a	0.0904	0.1089	<i>R</i> ₁ = 0.1185
<i>wR</i> ₂ (all data) ^b	0.1377	0.2792	<i>wR</i> ₂ = 0.1291
Largest difference in peak and hole (e Å ⁻³)	0.187 and -0.308	1.248 and -0.444	0.193 and -0.360

^a *R*₁ = Σ|*F*_o - *F*_c|/Σ|*F*_o|.

^b *wR*₂ = [Σ *w*(*F*_o² - *F*_c²)²/Σ *w*(*F*_o²)^{1/2}].

Table 4
Selected bond lengths (Å) and angles (°) for compounds L², Ni(L²)₂ and L³.

L ²					
C1–C2	1.372(4)	C2–C1–N1	109.6(2)	N3–C15–C16	124.8(2)
C1–N1	1.390(3)	C2–C1–C9	128.4(3)	N2–C16–C15	115.6(2)
C2–N3	1.390(3)	N1–C1–C9	121.9(2)	C16–N2–S1	123.7(2)
N1–C15	1.321(3)	C1–C2–N3	105.7(2)	C15–N3–C2	107.4(2)
C15–N3	1.360(3)	C1–C2–C3	129.8(3)	C15–N3–C24	126.9(2)
C15–C16	1.493(4)	N3–C2–C3	124.0(2)	C2–N3–C24	125.4(2)
C16–N2	1.459(4)	C15–N1–C1	106.0(2)	N3–C24–C25	113.1(2)
N3–C24	1.467(3)	N1–C15–N3	111.3(2)	N4–C25–C24	112.8(2)
C24–C25	1.509(4)	N1–C15–C16	123.9(2)		
C25–N4	1.470(4)				
Ni(L ²) ₂					
Ni1–N1	1.935(5)	C41–N7	1.342(8)	N4–C25–C24	113.0(6)
Ni1–N5	1.954(5)	C42–C49	1.364(9)	N5–C40–C41	105.5(5)
Ni1–N6	1.983(5)	C42–N6	1.380(8)	N6–C41–N7	110.8(5)
Ni1–N2	2.004(6)	C49–N7	1.399(8)	N6–C41–C40	120.3(6)
C8–C9	1.480(9)	C56–N7	1.463(8)	N7–C41–C40	128.8(6)
C8–N1	1.481(8)	C56–C57	1.511(10)	C49–C42–N6	108.9(5)
C9–N2	1.315(8)	C57–N8	1.462(9)	C42–C49–N7	106.1(5)
C9–N3	1.362(8)	N1–Ni1–N5	138.0(2)	N7–C56–C57	113.9(6)
C10–C17	1.366(9)	N1–Ni1–N6	128.7(2)	N8–C57–C56	111.1(5)
C10–N2	1.399(8)	N5–Ni1–N6	81.7(2)	C9–N2–C10	107.1(5)
C17–N3	1.400(8)	N1–Ni1–N2	82.1(2)	C9–N3–C17	107.1(5)
C24–N3	1.455(8)	N5–Ni1–N2	126.2(2)	C9–N3–C24	126.5(5)
C24–C25	1.506(10)	N6–Ni1–N2	98.6(2)	C17–N3–C24	126.3(5)
C25–N4	1.448(9)	N2–C9–N3	110.9(5)	C41–N6–C42	106.9(5)
C40–N5	1.459(8)	C17–C10–N2	108.6(5)	C41–N7–C49	107.3(5)
C40–C41	1.488(9)	C10–C17–N3	106.3(5)	C41–N7–C56	126.1(5)
C41–N6	1.327(8)	N3–C24–C25	113.1(6)	C49–N7–C56	126.6(5)
L ³					
C1–C2	1.376(3)	N2–C17	1.411(3)	C2–C1–N1	104.3(2)
C1–N1	1.388(3)	C17–N3	1.308(3)	C1–C2–N3	111.5(2)
C1–C9	1.472(3)	C17–N2–C16	106.0(2)	C17–N1–C1	106.82(19)
C2–N3	1.410(3)	N3–C17–N1	114.9(2)	C17–N1–C15	111.9(2)
N1–C17	1.345(3)	N3–C17–N2	134.5(2)	C1–N1–C15	137.0(2)
N1–C15	1.455(3)	N1–C17–N2	110.3(2)	N1–C15–C16	101.1(2)
C15–C16	1.524(4)	C17–N3–C2	102.4(2)	N2–C16–C15	104.39(19)
C16–N2	1.500(3)				

plied by using the multi-scan program SADABS [27]. All of the structures were solved by direct methods using the Program SHELXS-97 [28] and refined by the full-matrix least-squares methods on all *F*² data with SHELXL-97 [29]. The program PLATON [30] was used to check the result of the X-ray analysis and the program ORTEP [31] used to give a representation of the structures. H atoms on C atoms were placed in calculated positions. Experimental details for the structure analysis of L², Ni(L²)₂ and L³ are given in Table 3. The selected bond distances and angles for L², Ni(L²)₂ and L³ are listed in Table 4.

Supplementary material

CCDC 744553, 744554 and 744555 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgments

The authors thank the financial support by National Natural Science Foundation of China (Grant No. 20962003), Guangxi Natural Science Foundation (Grant No. 0991008) and Innovation Project of Guangxi Graduate Education (2009106020703M43).

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