Synthesis and Characterization of a Series of New Asymmetric Salphen Mono- and Binuclear Metal Complexes

Li, Jiayuan(李佳媛)　Guo, Liqin(郭莉芹)　Ruan, Wenjuan*(阮文娟)
Zhu, Zhiang(朱志昂)

Department of Chemistry, Nankai University, Tianjin 300071, China

Two novel asymmetric salen ligands H_2L^1 [*N*-phenyl-*N*-(2-hydroxy-5-methylphenyl)-*N'*-(2-hydroxy-3-methoxylphenyl)-*o*-phenyldiamine] and H_2L^2 [*N*-phenyl-*N*-(2-hydroxy-5-chlorophenyl)-*N'*-(2-hydroxy-3-methoxylphenyl)-*o*-phenyldiamine] and their metal complexes ML^n (M＝Zn, Co, Ni, Cu; n＝1, 2) have been prepared and characterized by elemental analyses, ^{1}H NMR, ESI-MS, FT-IR and UV-Vis spectra. In particular, the complex ZnL^1, the binuclear monosalphen complex, was synthesized and studied in detail using ^{1}H NMR and ESI-MS techniques. For other metal complexes under the same reaction conditions, only mononuclear complexes were obtained. The results are relevant to both the metal ions and the structure of ligands.

Keywords binuclear and mononuclear salphen complexes, synthesis, NMR spectroscopy, UV/Vis spectroscopy, IR spectroscopy

Introduction

Inspired from the structure of porphyrin, salen is developed as a tetradentate Schiff base system. Salens and their metal complexes have been investigated in a variety of applications because of their ease of preparation, diverse structure, low-cost, and so on. With the lone-pair electron afforded by the basic structure of C＝N structure, salen complexes have been of interest for their bioactivity,[1,2] and can identify both imidazole, pyridine, amino acids and other nitrogen-containing small molecules and complex molecular system such as carbohydrates, DNA molecules.[3-5] Most notably, they have been found to be of great utility in the development of chiral catalysts, and have been used to increase the stereoselectivity of products in a variety of reactions including asymmetric nitroaldol reaction,[6,7] asymmetric epoxidation,[8-10] ring-opening of epoxides, and so on.

Under the background of energy conservation, security and green chemistry, the efficient and recyclable catalyst of salen type becomes an on-going research focus.[11-13] In order to prevent the loss of active site of catalyst of small molecules via oxidation reaction generating oxygen-bridged dimer of the μ-oxo-Mn(IV), to design novel structures of salen complexes that can more effectively improve the reaction yield and selectivity is an urgent need to be addressed in addition to immobilized catalyst on the carrier.[14] Both simulation of biocatalysis and industrial asymmetric catalytic oxidation need asymmetric catalyst, so the synthesis of new asymmetric salen metal complexes has great significance. Besides, when the metal ions of the center of the salen complexes are different, the oxidation-reduction potential, non-linear optical property and other properties will change, which provide us with vast design space.

In this paper, we synthesized and characterized two novel salen ligands H_2L^1 [*N*-phenyl-*N*-(2-hydroxy-5-methylphenyl)-*N'*-(2-hydroxy-3-methoxylphenyl)-*o*-phenyldiamine] and H_2L^2 [*N*-phenyl-*N*-(2-hydroxy-5-chlorophenyl)-*N'*-(2-hydroxy-3-methoxylphenyl)-*o*-phenyldiamine] and their asymmetric metal complexes ML^n (M＝Zn, Co, Ni, Cu; n＝1, 2), as shown in Scheme 1. Both the right part of the ligands are fixed using *o*-vanillin, but we use ketone having different substituent in the left part to change the electronic environment of the part, thus change the electronic environment of the whole molecules.

Experimental

Materials and chemicals

N,*N*-Dimethyl formamide (DMF) and chloroform ($CHCl_3$) were purified by standard methods, while the other solvents were analytical grade and used as received. *o*-Phenylenediamine was purified by standard methods. Zinc(II) acetate, nickel(II) acetate, cooper(II) acetate, cobalt(II) acetate and the other reagents were commercial products used without further purification.

Physical measurements

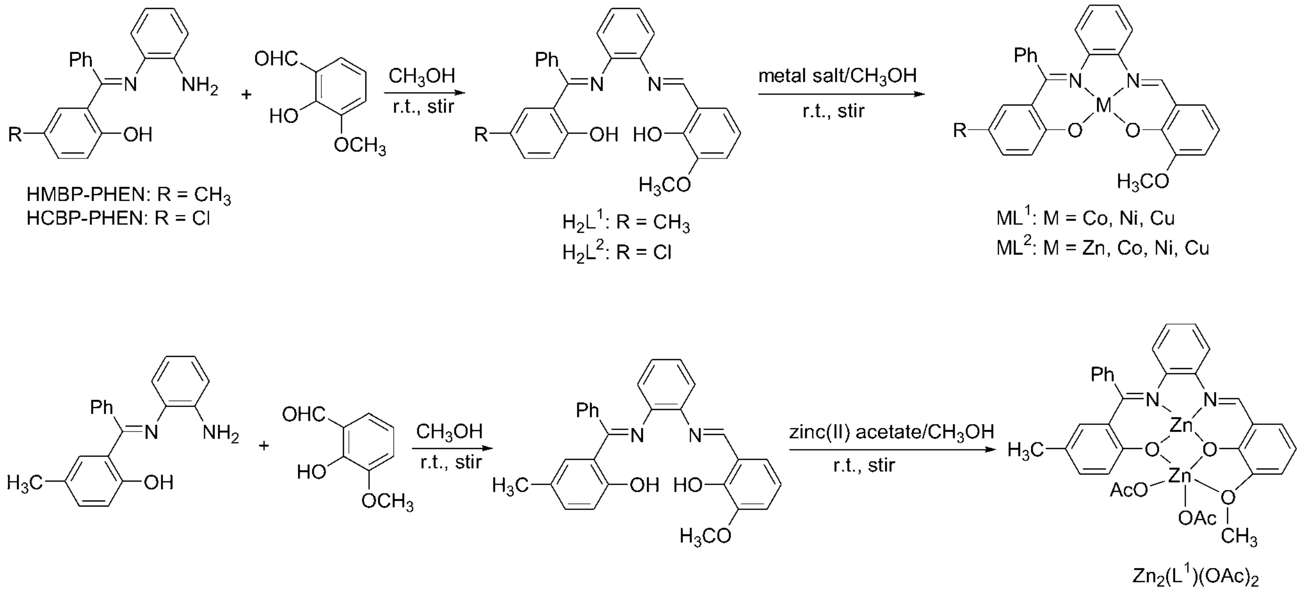
^{1}H NMR spectra were recorded on a Bruker AV300

---

* E-mail: wjruan@nankai.edu.cn

Received September 12, 2009; revised and accepted February 26, 2010.
Project supported by the National Natural Science Foundation of China (No. 20671053).

Scheme 1 Synthesis of ligands H_2L^1 and H_2L^2 and their metal complexes



NMR spectrometer (300 MHz), using Me_4Si as internal standard. Elemental (C, H and N) analyses were carried out with a Perkin-Elmer 240C elemental analyzer. FT-IR spectra were performed on a Shimadzu IR-408 infrared spectrophotometer in the range of 4000—400 cm^{-1}. Electrospray mass spectra (ESI-MS) were recorded on a Trace DSQ instrument. UV-Vis spectra were measured on a UV-2450 spectrophotometer with a thermostated cell compartment TCC-240A in the range of 200—600 nm using solutions with the concentration of 1×10^{-5} mol/L in DMF.

Synthesis of H_2L^n (n=1, 2)

The ligand H_2L^1 (or H_2L^2) was prepared according to the literature method[15] with some modifications. 2.0 mmol of HMBP-PHEN (or HCBP-PHEN) was suspended in hot methanol (30 mL). 0.3043 g (2.0 mmol) of *o*-vanillin was added to the suspension stepwise under stirring. After the addition was completed, the mixture was stirred and refluxed for 8 h. The orange product precipitated from solution. The solution was allowed to cool to room temperature and the products were collected by filtration. The orange solid was purified by chromatography on silica gel column using dichloromethane as eluent and dried in vacuum.

H_2L^1: Yield 86%. ^{1}H NMR ($CDCl_3$) δ: 2.130 (s, 3H, CH_3), 3.885 (s, 3H, OCH_3), 6.751 (t, J=4.2 Hz, 1H, Ar-H), 6.779 (s, 1H, Ar-H), 6.863 (t, J=8.1 Hz, 1H, Ar-H), 6.977 (t, J=9.3 Hz, 4H, Ar-H), 7.036—7.068 (m, 2H, Ar-H), 7.097 (d, J=8.1 Hz, 2H, Ar-H), 7.138 (s, 1H, Ar-H), 7.203 (t, J=8.1 Hz, 2H, Ar-H), 7.257—7.338 (m, 1H, Ar-H), 8.354 (s, 1H, CH=N), 13.085 (s, 1H, OH); ESI-MS *m/z* (%): 437.3 (100, $[M+H]^+$), 894.8 (100, $[2M+Na]^+$). Anal. calcd for $C_{28}H_{24}N_2O_3$: C 77.04, H 5.54, N, 6.42; found C 76.43, H 5.32, N 6.94.

H_2L^2: Yield 85%. ^{1}H NMR ($CDCl_3$) δ: 3.911 (d, J=10.2 Hz, 3H, OCH_3), 6.777 (t, J=4.8 Hz, 1H, Ar-H), 6.876 (t, J=7.5 Hz, 1H, Ar-H), 6.939 (s, 1H, Ar-H), 6.965 (s, 1H, Ar-H), 7.004 (q, J=3.9 Hz, 3H, Ar-H), 7.077 (d, J=6.6 Hz, 4H, Ar-H), 7.213 (t, J=7.2 Hz, 2H, Ar-H), 7.276 (d, J=2.7 Hz, 1H, Ar-H), 7.306 (d, J=2.4 Hz, 1H, Ar-H), 8.319 (s, 1H, CH=N), 13.068 (s, 1H, OH); ESI-MS *m/z* (%): 457.3 (100, $[M+H]^+$). Anal. calcd for $C_{27}H_{21}ClN_2O_3$: C 70.97, H 4.63, N 6.13; found C 70.50, H 4.51, N 6.13.

Synthesis of ML^n (M=Zn, Co, Ni, Cu)

General method 0.2 mmol of ligand H_2L^n was dissolved in 30 mL of hot methanol, and 0.6 mmol of metal acetate salt in 5 mL of methanol was added dropwise under stirring. After the addition was completed, the mixture was stirred at room temperature. The reaction was monitored by TLC until disappearance of all ligands was observed. The solvent was evaporated under vacuum to obtain the solid. The solid was purified by chromatograph on silica gel column and dried in vacuum.

CuL^1: Eluent: dichloromethane. Color: brown. Yield 53%. IR (KBr) v: 573.28, 538.04 (M—O), 487.43, 427.28 (M—N) cm^{-1}; ESI-MS *m/z* (%): 498.3 (100, $[M+H]^+$), 1017.0 (100, $[2M+Na]^+$). Anal. calcd for $C_{28}H_{22}N_2CuO_3\cdot4H_2O$: C 58.99, H 5.30, N 4.91; found C 58.63, H 5.01, N 4.36.

CuL^2: Eluent: chloroform. Color: brown. Yield 54%. IR (KBr) v: 575.90, 539.21 (M—O), 489.66 (M—N) cm^{-1}; ESI-MS *m/z* (%): 518.2 (100, $[M+H]^+$), 1036.7 (100, $[2M+H]^+$), 1058.8 (100, $[2M+Na]^+$). Anal. calcd for $C_{27}H_{19}ClN_2CuO_3\cdot5H_2O$: C 53.29, H 4.80, N 4.60; found C 53.13, H 4.75, N 4.60.

NiL^n: The brown solid was redissolved completely in $CHCl_3$, washed with water three times and dried in vacuum before purified by chromatograph on silica gel column using chloroform as eluent. Brown power was obtained.

NiL^1: Yield 45%. ^{1}H NMR ($CDCl_3$) δ: 1.982 (s, 3H, CH_3), 3.757 (s, 3H, OCH_3), 6.066 (t, J=8.4 Hz, 1H, Ar-H), 6.448—6.534 (m, 3H, Ar-H), 6.640 (d, J=7.2 Hz, 1H, Ar-H), 6.844 (q, J=8.4 Hz, 2H, Ar-H), 6.940 (d, J=8.1 Hz, 2H, Ar-H), 7.015 (d, J=8.7 Hz, 2H, Ar-H), 7.368—7.474 (m, 5H, Ar-H), 8.067 (s, 1H, CH=N); IR (KBr) ν: 578.20, 542.90 (M—O), 449.62, 410.06 (M—N) cm^{-1}; ESI-MS *m/z* (%): 493.3 (100, $[M+H]^+$), 515.2 (100, $[M+Na]^+$), 1007.0 (100, $[2M+Na]^+$). Anal. calcd for $C_{28}H_{22}N_2NiO_3•4H_2O$: C 59.50, H 5.35, N 4.96; found C 60.01, H 5.29, N 4.66.

NiL^2: Yield 46%. ^{1}H NMR ($CDCl_3$) δ: 3.788 (d, J=21.9 Hz, OCH_3), 6.050 (d, J=8.7 Hz, 1H, Ar-H), 6.464—6.528 (m, 2H, Ar-H), 6.646 (d, J=7.2 Hz, 1H, Ar-H), 6.658 (s, 1H, Ar-H), 6.744 (s, 1H, Ar-H), 6.808—6.948 (m, 2H, Ar-H), 7.011 (d, J=8.4 Hz, 3H, Ar-H), 7.393—7.479 (m, 4H, Ar-H), 8.052 (s, 1H, CH=N); IR (KBr) ν: 575.01, 543.53 (M—O), 451.49, 410.98 (M—N) cm^{-1}; ESI-MS, *m/z* (%): 513.2 (100, $[M+H]^+$), 1026.8 (100, $[2M+H]^+$), 1048.8 (100, $[2M+Na]^+$). Anal. calcd for $C_{27}H_{19}ClN_2NiO_3•2H_2O$: C 59.00, H 4.22, N 5.10; found C 59.05, H 4.29, N 5.27.

ZnL^n 0.2 mmol of ligand H_2L^n was dissolved in 30 mL of hot methanol, and 0.1749 g (0.6 mmol) of zinc(II) acetate in 10 mL of methanol was added dropwise. The mixture was stirred at room temperature for 12 h. Then the solvent was removed under vacuum to obtain a yellow solid. The solid was washed with hot methanol and water three times respectively, and dried in vacuum.

$Zn_2(L^1)(OAc)_2$: Yield 46%. ^{1}H NMR (DMSO-d_6) δ: 1.777 (s, 6H, OAc), 1.964 (s, 3H, CH_3), 3.730 (s, 3H, OCH_3), 6.438 (q, J=7.5 Hz, 2H, Ar-H), 6.682 (t, J=8.1 Hz, 2H, Ar-H), 6.823 (t, J=8.4 Hz, 2H, Ar-H), 6.971—7.070 (m, 3H, Ar-H), 7.219 (s, 2H, Ar-H), 7.400 (s, 3H, Ar-H), 7.542 (d, J=7.8 Hz, 1H, Ar-H), 8.830 (s, 1H, CH=N); IR (KBr) ν: 576.42, 530.44 (M—O), 487.80 (M—N) cm^{-1}; ESI-MS *m/z* (%): 701.9 (100, $[M+H]^+$). Anal. calcd for $C_{28}H_{22}N_2Zn_2O_3•2OAc•2H_2O$: C 53.43, H 4.48, N 3.89; found C 52.15, H 4.22, N 3.67.

ZnL^2: Yield 48%. ^{1}H NMR (DMSO-d_6) δ: 3.732 (s, 3H, OCH_3), 6.415 (t, J=7.2 Hz, 1H, Ar-H), 6.506 (d, J=9.0 Hz, 1H, Ar-H), 6.826 (q, J=8.4 Hz, 4H, Ar-H), 6.992 (d, J=8.4 Hz, 1H, Ar-H) 7.083—7.185 (m, 2H, Ar-H), 7.283 (s, 2H, Ar-H), 7.435 (s, 2H, Ar-H), 7.565 (d, J=7.5 Hz, 1H, Ar-H), 8.844 (s, 1H, CH=N); IR (KBr) ν: 587.74, 530.44 (M—O), 490.48, 412.40 (M—N) cm^{-1}; ESI-MS *m/z* (%): 521.2 (100, $[M+H]^+$), 1041.0 (100, $[2M+H]^+$). Anal. calcd for $C_{27}H_{19}ClN_2ZnO_3•5H_2O$: C 63.13, H 4.79, N 4.59; found C 62.82, H 4.22, N 4.31.

CoL^n 0.2 mmol of ligand H_2L^n was dissolved in 30 mL of hot methanol, and 0.1494 g (0.6 mmol) of cobalt(II) acetate in 10 mL of methanol was added dropwise under nitrogen protection. After the addition was completed, the mixture was stirred at room temperature for 12 h. The reaction was monitored by TLC until disappearance of all ligand was observed. The solvent was evaporated under vacuum to obtain a deep red solid. The deep red solid was purified by chromatography on silica gel column and dried in vacuum.

CoL^1: Eluent: dichloromethane. Yield 43%. IR (KBr) ν: 578.81, 540.79 (M—O), 487.80, 445.61 (M—N) cm^{-1}; ESI-MS *m/z* (%): 493.2 (100, $[M+H]^+$), 986.0 (100, $[2M+H]^+$). Anal. calcd for $C_{28}H_{22}N_2CoO_3•6H_2O$: C 55.91, H 5.70, N 4.66; found C 55.82, H 5.61, N 4.42.

CoL^2: Eluent: chloroform. Yield 42%. IR (KBr) ν: 576.08, 542.01 (M—O), 463.52, 431.58 (M—N) cm^{-1}. ESI-MS *m/z* (%): 513.2 (100, $[M+H]^+$), 1031.8 (100, $[2M+H]^+$). Anal. calcd for $C_{27}H_{19}ClN_2CoO_3•5H_2O$: C 53.70, H 4.84, N 4.64; found C 54.47, H 4.44, N 4.44.

Results and discussion

^{1}H NMR

The data of the ^{1}H NMR in $CDCl_3$ or DMSO-d_6 are given in Table 1. The data of H_2L^n shows characteristic peak of azomethine (CH=N) as singlet at about δ 8.4 and proton of hydroxy group at about δ 13.0. Integration of peak area and the value of the chemical shifts are in line with the target compounds (Schiff base). This indicates the reaction of aldehyde and amine to generated ligands effectively. Moreover, the characteristic peaks of hydroxy group of metal complexes can not be found which proves the occurrence of coordination reaction as well as the purity of the product.

The structure of complex $Zn_2(L^1)(OAc)_2$ is shown in Figure 1. The data of the ^{1}H NMR in DMSO-d_6 are given in experimental section. The ^{1}H NMR spectrum of $Zn_2(L^1)(OAc)_2$ shows characteristic peak of acetate (OAc) as singlet at about δ 1.777 and the result, 6H, of integration of peak area and chemical shifts is consistent with the data of ESI-MS (701.9). This indicates that the structure of the compound is the same as we presumed and is also in line with the literature.[16] The isolation of bimetallic monosalphen structures is relevant to both the transmetalation of Zn(salen) complexes and the structure of salen ligands.[16] Containing *o*-pheylenediamine which forms a rigidity of the salphen system increasing Lewis acidity behavior of the Zn(II) ion and *o*-vanillin leading the salen complexes equipped with additional alkoxy donor groups at the 3-position of the salicylideneimine groups, the Zn(II) ion allows the ligation of an axial ligand OAc. But as a result of the effect of the substituent of chlorine, the complex ZnL^2 did not form such compound.

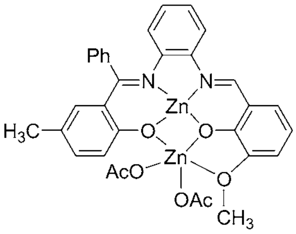


Figure 1 Structure of complex $Zn_2(L^1)(OAc)_2$.

Table 1 Some ^{1}H NMR chemical shift (δ) data of ligands and their complexes

Compd.	OH	CH＝N	OCH_3	CH_3	OAc
H_2L^1	13.085 (s, 1H)	8.354 (s, 1H)	3.885 (s, 3H)	2.130 (s, 3H)	
$Zn_2(L^1)(OAc)_2$		8.830 (s, 1H)	3.730 (s, 3H)	1.964 (s, 3H)	1.777 (s, 6H)
NiL^1		8.067 (s, 1H)	3.757 (s, 3H)	1.982 (s, 3H)	
H_2L^2	13.068 (s, 1H)	8.319 (s, 1H)	3.911 (d, J＝10.2 Hz, 3H)		
ZnL^2		8.844 (s, 1H)	3.732 (s, 3H)		
NiL^2		8.052 (s, 1H)	3.788 (d, J＝21.9 Hz, 3H)		

UV-Vis spectra

The UV-Vis spectra of all complexes in DMF were recorded in the region of 200—700 nm, as shown in Figures 2 and 3. Exhibiting three bands, the spectra at about 260 and 290 nm can be assigned to the π-π* transitions of aromatic ring and the azomethine (CH＝N) respectively, and peaks at about 350 nm are assigned to n-π* transitions.[17-19]

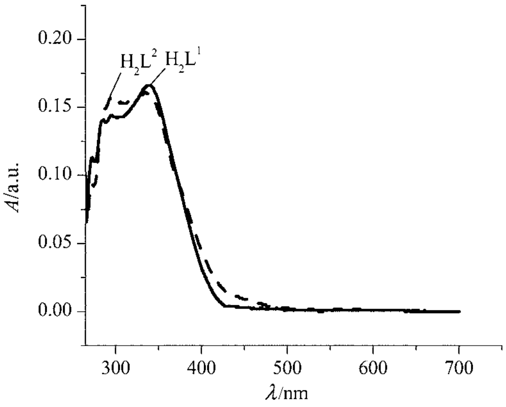


Figure 2 UV-Vis spectra of ligands H_2L^1 and H_2L^2 in DMF.

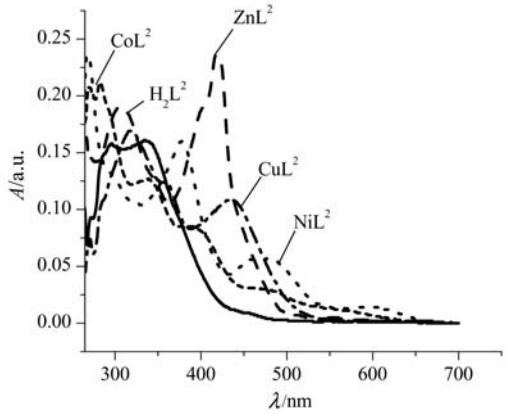


Figure 3 UV-Vis spectra of ligand H_2L^2 and its metal complexes ML^2 (M＝Zn, Co, Ni, Cu) in DMF.

It can be seen from Table 2 and Figures 2 and 3 that the spectrum of the free ligand H_2L^2 is similar to that of H_2L^1, but the peak at around 340 nm shifts to the short-wave direction by 5 nm, as a result of ligand H_2L^2 having a chloro-group, a weak acceptor, which lowered the density of electron cloud of benzene ring and magnified the orbital energy of n-π* transition. After complexation with metal ions, the spectra shows variations with respect to the position and intensity, compared with the spectra of their ligands. For salen metal complexes, initial peaks of π-π* transitions of azomethine (CH＝N) blue shift for the reason as follows. Although the charge density has been dispersed and the whole energy declines, the energy level difference between the bonding orbital and anti-bonding orbital of π-π* increases after the coordination of e-participation of C＝N. In addition, a new absorbtion band of the visible region should be attributed to metal-to-ligand charge-transfer character. The impact to the diversity of the spectra of the salen complexes involves the different metal center.

Table 2 UV-Vis spectra data of ligands and their complexes in DMF at room temperature

Compd.	λ/nm [ε/(10^4 L•mol^{-1}•cm^{-1})]
H_2L^1	273 (1.13), 286 (1.41), 296 (1.44), 340 (1.66)
H_2L^2	273 (0.93), 286 (1.47), 296 (1.58), 335 (1.61)
$Zn_2(L^1)(OAc)_2$	303 (1.63), 342 (1.27), 392 (1.11)
ZnL^2	307 (1.89), 402 (1.90), 419 (2.35)
CoL^1	274 (1.07), 355 (0.39), 424 (1.39), 520 (0.12)
CoL^2	284 (2.10), 338 (1.27), 390 (0.85), 478 (0.30)
NiL^1	268 (2.33), 282 (1.68), 375 (1.80), 462 (0.68), 590 (0.15)
NiL^2	269 (2.36), 379 (1.59), 470 (0.57), 599 (0.14)
CuL^1	318 (1.57), 363 (1.08), 425 (2.34), 560 (0.07)
CuL^2	271 (0.74), 318 (1.69), 359 (1.24), 436 (1.08)

IR spectra

Table 3 gives some IR data of ligands and their complexes. The band of IR spectra 1600—1620 and 1170—1200 cm^{-1} are assigned to $\nu_{C=N}$, and ν_{C-O} vibration respectively, which show band characteristic for salen ligands and complexes. This is good agreement with the literature.[20,21] The IR spectra show peaks around 1570 cm^{-1} assigned to benzene ring $\nu_{C=C}$ vibration, and round 1130 cm^{-1} assigned to ν_{C-N} vibration.[22] In addition, the coordination of the metal ions to ligands is supported by the appearance of peaks during 400 and 600 cm^{-1}. This indicates the reaction of aldehyde and amine generating ligands, then ligands and metal generating metal complexes effectively.

Table 3 Some IR data (ν/cm^{-1}) of the ligands and their complexes[a]

Compd.	C=N	Ph-ring C=C	C—O	C—N	M—O	M—N
H_2L^2	1607.31 (s)	1564.91 (s)	1173.94 (m)	1120.04 (m)	—	—
ZnL^2	1613.72 (s)	1572.07 (s)	1183.31 (s)	1118.98 (m)	587.74 (w) 530.44 (m)	490.48 (w) 412.40 (w)
CoL^2	1617.75 (s)	1575.84 (s)	1181.02 (s)	1130.03 (m)	576.08 (w) 542.01 (m)	463.52 (w) 431.58 (w)
NiL^2	1607.31 (s)	1578.40 (m)	1180.50 (m)	1147.91 (m)	575.01 (w) 543.53 (m)	451.49 (w) 410.98 (w)
CuL^2	1608.18 (s)	1576.38 (m)	1185.54 (s)	1145.34 (m)	575.90 (w) 539.21 (m)	489.66 (w)
H_2L^1	1610.23 (s)	1567.95 (s)	1188.95 (s)	1124.31 (m)	—	—
$Zn_2(L^1)(OAc)_2$	1616.39 (s)	1567.47 (s)	1184.20 (m)	1127.63 (w)	556.42 (w) 530.44 (w)	487.80 (w) —
CoL^1	1608.95 (s)	1578.07 (m)	1178.27 (m)	1145.20 (m)	578.81 (w) 540.79 (w)	469.68 (w) 445.61 (w)
NiL^1	1604.72 (s)	1577.70 (m)	1199.10 (m)	1144.43 (m)	578.20 (w) 542.90 (m)	449.62 (w) 410.06 (w)
CuL^1	1606.53 (s)	1573.97 (m)	1184.03 (m)	1142.46 (m)	573.28 (m) 538.04 (m)	487.43 (w) 427.28 (w)

[a] Abbreviations: s, strong; m, medium; w, weak.

Conclusions

In summary, we successfully synthesized a series of new salen-type asymmetric complexes and these compounds are characterized by elemental analysis, ^1H NMR, ESI-MS, FT-IR and UV-Vis spectra. In particular, the salen-type complex $Zn_2(L^1)(OAc)_2$, the binuclear mono-salphen complexes, was synthesized and studied in detail using ^1H NMR and ESI-MS techniques. For other metal complexes under the same reaction conditions, only mononuclear complexes were obtained. The results are relevant to both the metal ions and the structure of salen-type ligands.

References

1 Cini, R.; Moore, S. J.; Marzilli, L. G. *Inorg. Chem.* **1998**, *37*, 6890.
2 Polson, S. M.; Cini, R.; Pifferi, C.; Marzilli, L. G. *Inorg. Chem.* **1997**, *36*, 314.
3 Abe, A. M.; Helaja, J.; Koskinen, A. P. *Org. Lett.* **2006**, *8*, 4537.
4 Kim, H. J.; Kim, W.; Lough, A. J.; Kim, B. M.; Chin, J. *J. Am. Chem. Soc.* **2005**, *127*, 16776.
5 Klärner, F.-G.; Kahlert, B. *Acc. Chem. Res.* **2003**, *36*, 919.
6 Kowalczyk, R.; Kwiatkowski, P.; Skar, J.; Jurczak, J. *J. Org. Chem.* **2009**, *74*, 753.
7 Zulauf, A.; Mellah, M.; Schulz, E. *J. Org. Chem.* **2009**, *74*, 2242.
8 Atwood, D. A.; Harvey, M. J. *Chem. Rev.* **2001**, *101*, 37.
9 Reger, T. S.; Janda, K. D. *J. Am. Chem. Soc.* **2000**, *122*, 6929.
10 Haikarainen, A.; Sipila, J.; Pietikainen, P. *J. Chem. Soc., Dalton Trans.* **2001**, 991.
11 Thakur, S. S.; Li, W. J.; Shin, C. K.; Kim, G. J. *Chirality* **2006**, *18*, 37.
12 Thakur, S. S.; Chen, S. W.; Kim, G. J. *J. Organomet. Chem.* **2006**, *691*, 1862.
13 Li, W. J.; Thakur, S. S.; Chen, S. W. *Tetrahedron Lett.* **2006**, *46*, 2263.
14 Yang, H. Q.; Zhang, L.; Li, C. *Angew. Chem., Int. Ed.* **2007**, *46*, 6861.
15 Atkins, R.; Brewer, G. *Inorg. Chem.* **1985**, *24*, 127.
16 Feiices, L. S.; Benet, J. B. *Inorg. Chem.* **2009**, *48*, 846.
17 Boghaei, D. M.; Behzad, M. *Synth. React. Inorg. Met.-Org. Chem.* **2005**, *35*, 261.
18 Khandar, A. A.; Shaabani, B.; Belaj, F.; Bakhtiari, A. *Polyhedron* **2006**, *25*, 1893.
19 Rabie, U. M.; Assran, A. S. A.; Abou-El-Wafa, M. H. M. *J. Mol. Struct.* **2008**, *872*, 113.
20 Asadi, M.; Jamshid, K. A.; Kyanfar, A. H. *Inorg. Chim. Acta* **2007**, *360*, 1725.
21 Tas, E.; Kilic, A.; Konak, N.; Yilmaz, I. *Polyhedron* **2008**, *27*, 1024.
22 Pui, A.; Policar, C.; Mahy, J. P. *Inorg. Chim. Acta* **2007**, *360*, 2139.

(E0909121 Li, L.)