多胺配体及其配合物的合成与热力学性质研究

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摘要:合成并表征了 5 个多胺配体 *N*,*N*′-二(1,10-菲罗啉-2-亚甲基)-1,2-乙二胺(**L1**),1,7-二(1,10-菲罗啉-2-亚甲基)-1,4,7-三氮杂庚烷(**L2**),1,10-二(1,10-菲罗啉-2-亚甲基)-1,4,7,10-四氮杂癸烷(**L3**),1,13-二(1,10-菲罗啉-2-亚甲基)-1,4,7,10,13-五氮杂十三烷(**L4**),*N*,*N*′-二(1,10-菲罗啉-2-亚甲基)-1,3-丙二胺(**L5**)。利用 pH 电位滴定法在 25.0 ± 0.1 ℃时测定了这 5 个配体的质子化常数及其与 Co(Ⅱ),Ni(Ⅱ),Cu(Ⅱ)和 Zn(Ⅱ)形成配合物的稳定常数,并且试图解释了这 5 个系列配合物的差异。

关键词:多胺配体;过渡金属配合物;质子化常数;稳定常数
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Synthesis and Thermodynamic Properties of Five Multidentate Ligands and Their Complexes

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Abstract: Five multidentate ligands: *N*,*N*′ -di (1,10-phenanthroline-2-methylene)-1,2-ethylenediamine (**L1**),1,7-di(1,10-phenanthroline-2-methylene)-*n*-1,4,7-triazaheptane(**L2**), 1,10-di(1,10-phenanthroline-2-methylene)-*n*-1,4,7,10-tetraazadecane (**L3**), 1,13-di (1,10-phenanthroline-2-methylene)-*n*-1,4,7,10,13-pentaazatridecane (**L4**), *N*,*N*′ -di(1,10-phenanthroline-2-methylene)-1,3-diaminopropane(**L5**) were synthesized and characterized. The stability of the complexes of the five ligands with transition metal ions Co(Ⅱ), Ni(Ⅱ), Cu(Ⅱ) and Zn(Ⅱ) was studied by the potentiometric technique in water and I=0.1 mol·dm^{-3} KNO_3 at 25.0 ± 0.1 ℃, respectively. The difference among the five series of complexes is tentatively explained.

Key words: multidentate ligands; transition metal complexes; protonation constants; stability constants

1,10-Phenanthroline derivatives and their transition metal complexes have attracted considerable attention because of their novel structure and properties. In this paper, we report the synthesis and potentiometric properties of five new 1,10-phenanthroline derivatives and their complexes. The synthesis route and structure of the ligands are shown in Fig.1. The protonation constants of the ligands and the stability constants of complexes of the five ligands with transition metal ions Cu(Ⅱ), Ni(Ⅱ), Co(Ⅱ) and Zn(Ⅱ) were studied by means of pH titration.

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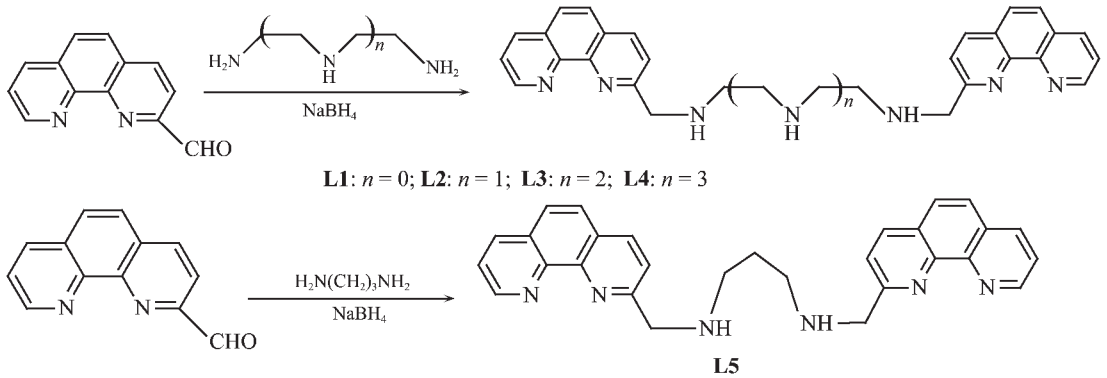


Fig.1 Synthesis route of the ligands **L1~L5**

1 Experimental

1.1 Reagents

All regents and solvents were of A.R. grade and were purified by standard techniques prior to use unless otherwise noted. All aqueous solution was prepared by redistilled water. 1,10-phenanthroline-2-formaldehyde was synthesized according to earlier reports[1~3]. The metal nitrates were purchased from Tianjin Third Chemical Reagent Factory and recrystalized. All the metal ion solutions were standardized with EDTA.

1.2 Instruments

Elemental analyses for C, H and N were carried out on a Perkin Elmer 240C element analyzer at the Institute of Elemental Organic Chemistry, Nankai University. IR spectra were recorded using Nicolet 170X-FTIR spectrometer. The ^{1}H NMR spectra were recorded using a Varian UNITY-plus 400 MHz spectrometer at Ministry of Education Key Laboratory of Functional Polymer Materials, Nankai University. The potentiometric titration were processed by means of a Beckman Φ 71 pH instrumen-tal equipped with a 39841 combination electrode.

1.3 Potentiometric determination

Potentiometric determination was measured in a 25 mL jacketed cell thermostated at 298.2 ± 0.1 K by a refrigerated water bath. Anaerobic conditions were maintained using pre-purified N_2 as an inert atmosphere, and ionic strengths were adjusted by adding KNO_3 to achieve I=0.1 mol·dm^{-3}. The calibration of the glass electrode was the same as described in the literature[4]. The concentration of the ligand in the experimental solutions (for molar ratios M:L of 2:1 binary system) was 5×10^{-4} mol·dm^{-3}. The calculations of the protonation and stablity constants were made using the SCMAR program[5] based on the improved TITFIT technique[6]. In each system, three independent titrations must be performed and 50 points should be recorded for each titration.

1.4 Synthesis of *N*, *N*′-di(1, 10-phenanthroline-2-methylene)-1, 2-ethylenediamine (L1)-N,N′-di (1,10-phenanthroline-2-methylene)-1,3-diaminopropane (L5)

10 mmol 1,10-phenanthroline-2-formaldehyde in 50 mL anhydrous methanol was added dropwise to an anhydrous methanol solution (50 mL) containing 5 mmol ethylenediamine, di-ethylene-triamine, tri-ethylene-tetra-amine, tetra-ethylene-penta-amine, 1,3-diaminopropane, respectively. The mixture was kept stirring for 12 h at room temperature, then cooled to 0 ℃ using an ice-water bath. 1.0 g $NaBH_4$ was then slowly added to the solution. After the addition, another 12 h stirring was maintained. The yellow solid was obtained after the solvent removal by evaporation. 50 mL water was added to the yellow residue, then stirred for 30 min. The mixture was filtered and the remaining solid was collected and dried. Dissolve the solid in 50 mL anhydrous alcohol and adjust the pH to 2 ~3 with concentrate HCl. A large amount of white solid was harvested. The product **L1 ~L5**′ s hydrochl-oride was obtained by filtration. Yield: 65%~80%.

1.5 ^{1}H NMR, IR spectra and elemental analysis of L1~L5

L1: ^{1}H NMR (D_2O) δ: 8.96 (t, 4H, phen), 8.50(d,

2H phen), 8.02(m, 6H, phen), 7.78(d, 2H, phen), 4.81 (s, 4H, phen-CH_2-), 3.86 (d, 4H, -CH_2-NH-). IR: 3 440 (ν_{N-H}), 1 495(δ_{CNH}), 1 556(δ_{CNH}), 1 595, 1 353, 850 ($\nu_{phen-ring}$). Molecular formula: $C_{28}N_6H_{24}\cdot 4HCl\cdot 8H_2O$. calcd.(%): C 45.75, H 6.04, N 11.44; found (%): C 45.81, H 5.96, N 11.34.

L2: ^{1}H NMR (D_2O) δ: 9.01 (d, 4H, phen), 8.58(d, 2H, phen), 8.13(m, 6H, phen), 7.85(d, 2H, phen), 4.91 (s, 4H, phen-CH_2), 3.81 (t, 8H,-CH_2-NH-). IR: 3 440 (ν_{N-H}), 1 509(δ_{CNH}), 1 558(δ_{CNH}), 1 600, 1 350, 862($\nu_{phen-ring}$). Molecular formula: $C_{30}N_7H_{29}\cdot 5HCl\cdot 2H_2O$. calcd. (%): C 51.00, H 5.42, N 13.88; found (%): C 51.07, H 4.98, N 14.21.

L3: ^{1}H NMR (D_2O) δ: 9.18(m, 4H, phen), 8.72(d, 2H, phen), 8.25(m, 6H, phen), 7.89(d, 2H, phen), 4.98 (s, 4H, phen-CH_2-), 3.85(t, 8H, -CH_2-NH-), 3.76(t, 4H, -CH_2-NH-). IR: 3 450 (ν_{N-H}), 1 510 (δ_{CNH}), 1 556 (δ_{CNH}), 1 600, 1 350, 862 ($\nu_{phen-ring}$). Molecular formula: $C_{32}N_8H_{34}\cdot 6HCl\cdot 9H_2O$. calcd. (%): C 42.13, H 6.41, N 12.29; found(%): C 42.15, H 5.96, N 11.99.

L4: ^{1}H NMR (D_2O) δ: 9.33 (t, 4H, phen), 8.67(d, 2H, phen), 8.30(m, 6H, phen), 8.05(d, 2H, phen), 5.01 (s, 4H, phen-CH_2-), 3.88(t, 8H, -CH_2-NH-), 3.75(t, 8H, -CH_2-NH-). Molecular formula: $C_{34}N_9H_{39}\cdot 7HCl\cdot 17H_2O$. calcd.(%): C 35.94, H 7.10, N 11.10; found (%): C 36.37, H 6.84, N 10.62.

L5: ^{1}H NMR (D_2O) δ: 9.13 (t, 4H, phen), 8.55(d, 2H, phen), 8.22(d, 2H, phen), 8.17(d, 4H, phen), 7.86 (d, 2H, phen), 4.85(s, 4H, phen-CH_2-), 3.60(t, 4H,-CH_2-NH-), 2.57 (m, 2H, -CH_2-NH-). IR: 3 451(ν_{N-H}), 1 502 (δ_{CNH}), 1 559(δ_{CNH}), 1 588, 1 346, 852($\nu_{phen-ring}$). Molecular formula: $C_{29}N_6H_{26}\cdot 4HCl\cdot 2H_2O$. calcd.(%): C 54.35, H 5.35, N 13.12; found(%): C 54.01, H 5.22, N 12.71.

2 Results and discussion

2.1 Protonation constants of L1~L5

In the pH range studied (2.5~10.8), the stepwise protonation constants of the five ligands were measured by potentiometric technique in water at 25.0 ± 0.1 ℃ and I=0.1 mol·dm^{-3} KNO_3. The equaibrium in the system can be written as in Equation (**1**). The accumulted protonation or equilibrilium constants $\beta_{mlh}=C_{M_mL_lH_h}/(C_M^m C_L^l C_H^h)$, where m, l and h are the molar totals of the transition metal ions, the ligands and the hydrogen ions, respectively, and m is equal to zero when the protonation constants is titrated. The results are listed in Table 1. Species distribution curves are shown in Fig.2.

$$mM + lL + hH \rightleftharpoons M_mL_lH_h \quad (1)$$

In our work, these ligands should exhibit protonation constants varying from 4 to 7, theoretically ligands **L1**, **L5**, **L2**, **L3**, **L4** should exhibit six, six, seven, eight, nine protonation constants, because in two nitrogen atoms of 1,10-phenanthroline only one nitrogen atom can be combined with protons, and the calculated results indicate that ligands **L1**, **L5**, **L2**, **L3**, **L4** exhibit four, four, five, six, seven protonation constants. From Fig.1, it can also see that the order for each step protonation constant from **L1** to **L5** is **L1** < **L5** < **L2** < **L3** < **L4**, due to the π-conjugation system

Table 1　Protonation constants for the ligands: L1~L5

	lgβ_1	lgβ_2	lgβ_3	lgβ_4	lgβ_5	lgβ_6	lgβ_7
L1	8.85	15.12	19.23	21.91	—	—	—
L2	9.45	17.82	22.50	25.70	28.61	—	—
L3	9.76	18.53	24.58	28.34	31.31	32.62	—
L4	9.85	18.64	25.70	30.31	34.03	37.67	40.17
L5	9.06	16.70	20.87	24.00	—	—	—
	lgK_1	lgK_2	lgK_3	lgK_4	lgK_5	lgK_6	lgK_7
L1	8.85	6.27	4.11	2.68	—	—	—
L2	9.45	8.37	4.68	3.20	2.91	—	—
L3	9.76	8.77	6.05	3.76	2.97	1.31	—
L4	9.85	8.79	7.06	4.61	3.72	3.64	2.50
L5	9.06	7.64	4.17	3.13	—	—	—

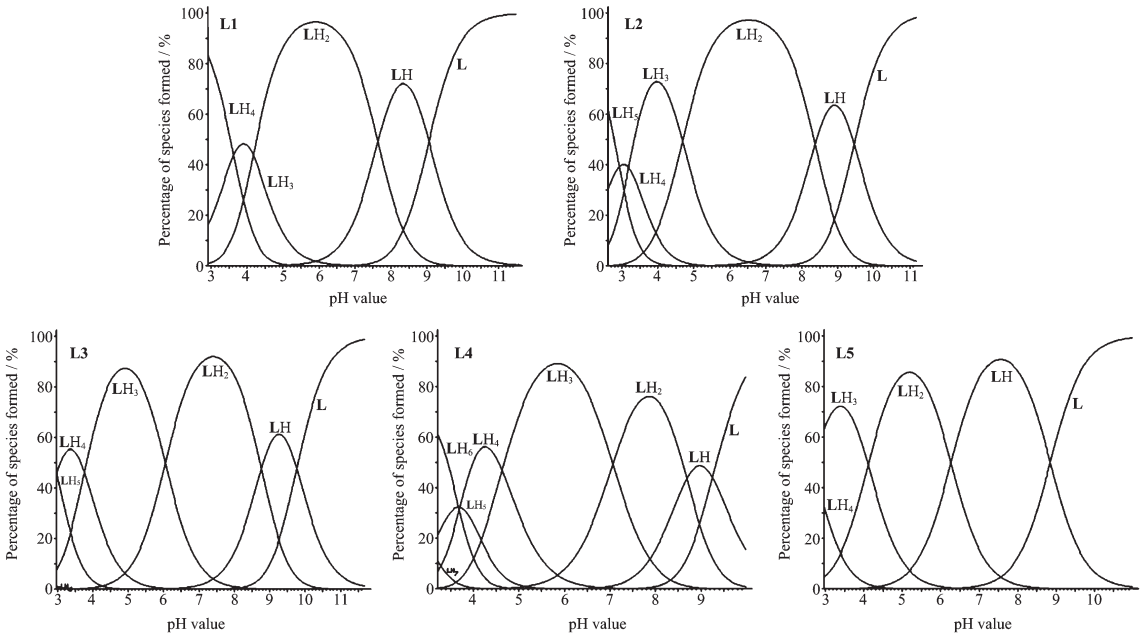


Fig.2 Protonation species distribution curves of the ligands

electron withdrawing character of 1,10-phenanthroline. The electron cloud density of nitrogen atom located near 1,10-phenanthroline is decreased. The more leaver from 1,10-phenanthroline, the larger is the electron cloud density of nitrogen atom. Therefore for ligand **L4**, the 7-site-nitrogen atom located at 1,4,7,10,13-pentaazatridecane exhibits the largest protonation constant. The 1,10-phenenthroline groups deprotonate at a lower pH and the amino groups deprotonate at higher pH, while, because of the effect of withdrawing electron from the already protonated ammonium ions, the stepswise protonation constants of these ligands will decrease successively.

2.2 Stability constants of complexes of the ligands with Co(Ⅱ), Ni(Ⅱ), Cu(Ⅱ) and Zn(Ⅱ)

Tables 2~6 show the stability constants ($\lg\beta_{mlh}$) of the five ligands, respectively. The species distribution curves of M**L** system are shown in Fig.3 (take Cu^{2+} for example). From the data of Tables 2~6, we can see that there exists the sequence of $Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$ in the stability constants, which is in agreement with the Ivring-William sequence. As is known, the stability constants of complexes mainly depend on the basicity of coordination atom. And as the increase of the electron-providing effect, the basicity of the amino is enhanced, therefore, the coordination capabilities of ligands with these metal ions show the sequence of M-**L1** < M-**L5** < M-**L2** < M-**L3** < M-**L4**. Because single crystal is not available in this work, the structures of these complexes shown in Fig.4 are proposed according to the rules of coordination of these ions.

Table 2 Stability constants for the ligand L1

	Co(Ⅱ)	Ni(Ⅱ)	Cu(Ⅱ)	Zn(Ⅱ)
$\lg\beta_{210}$	−3.46	1.63	2.71	2.67
$\lg\beta_{21-1}$	−13.65	−9.25	−7.27	−7.35
pK_a	10.19	10.88	9.98	10.02

Table 3 Stability constants for the ligand L2

	Co(Ⅱ)	Ni(Ⅱ)	Cu(Ⅱ)	Zn(Ⅱ)
$\lg\beta_{211}$	18.93	20.1	20.24	20.14
$\lg\beta_{210}$	10.77	11.19	11.38	11.18
$\lg\beta_{21-1}$	1.19	1.50	1.52	1.29
pK_a	9.58	9.69	9.86	9.89

Table 4 Stability constants for the ligand L3

	Co(Ⅱ)	Ni(Ⅱ)	Cu(Ⅱ)	Zn(Ⅱ)
$\lg\beta_{212}$	27.77	28.06	28.17	28.11
$\lg\beta_{211}$	22.44	23.75	23.81	22.78
$\lg\beta_{210}$	14.05	17.55	17.61	14.65
$\lg\beta_{21-1}$	4.65	8.87	8.94	5.27
pK_a	9.40	8.68	8.67	9.38

The coordination patterns of the complexes (Cu^{2+}:**L4**=2∶1 as an example) may be as follows. In the low pH range (pH about 2.5) the proton H^+ on the nitrogen

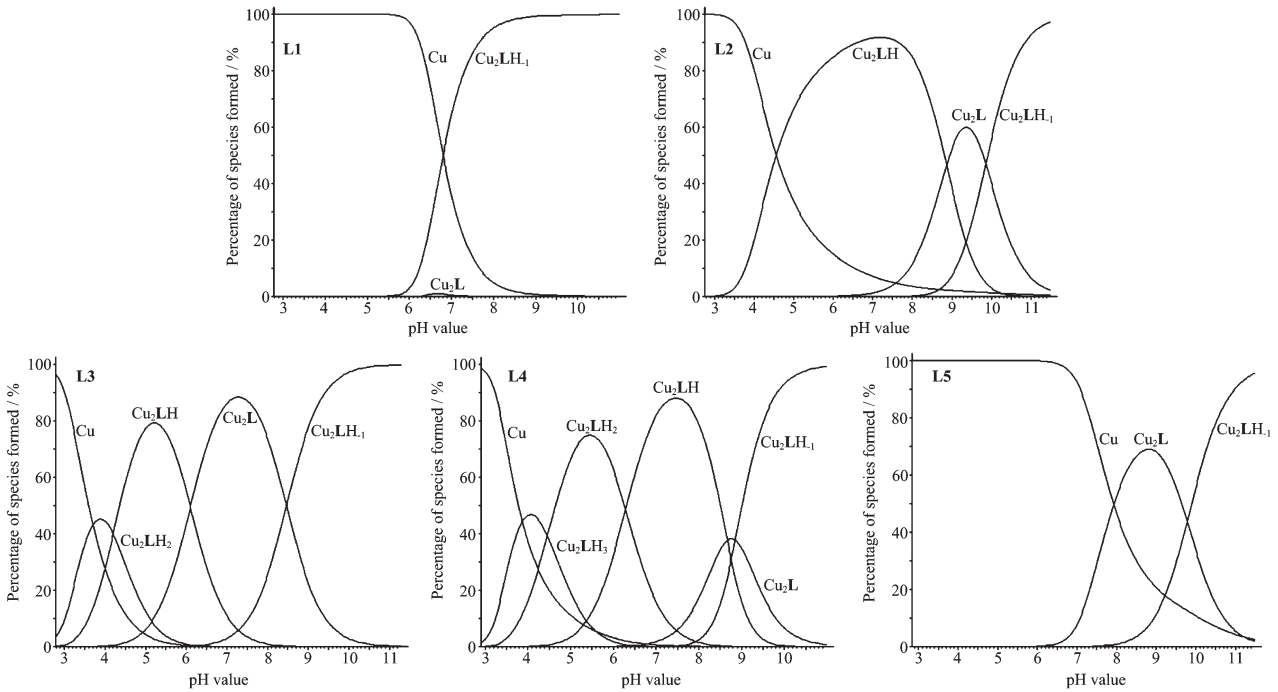
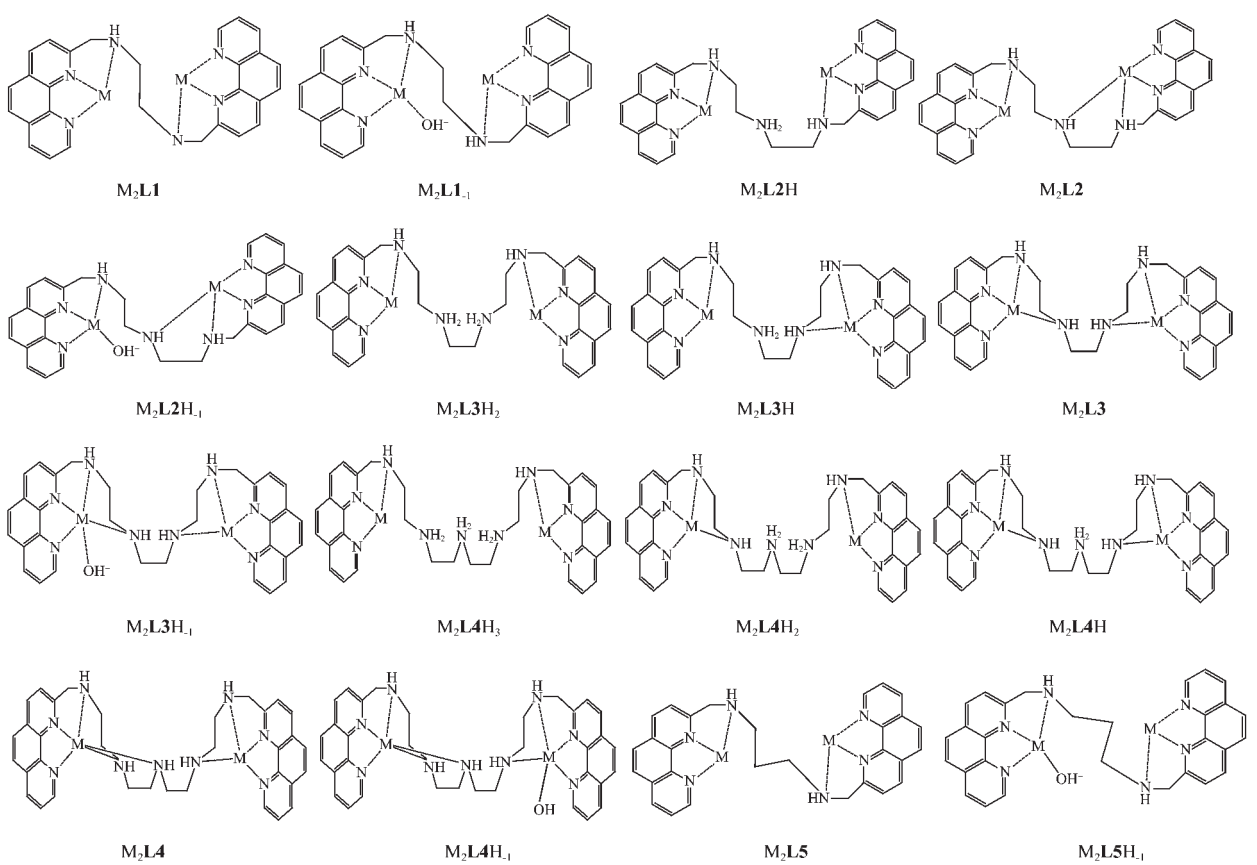


Fig.3　Distribution curves of the Cu(Ⅱ) complexes of the ligands **L1~L5** Cu(Ⅱ):**L**=2:1



M=Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}

Fig.4　Proposed structures for M:**L**=2:1 system

Table 5 Stablility constants for the ligand L4

	Co(Ⅱ)	Ni(Ⅱ)	Cu(Ⅱ)	Zn(Ⅱ)
$\lg\beta_{213}$	31.80	32.55	32.9	32.68
$\lg\beta_{212}$	27.07	27.38	28.44	28.38
$\lg\beta_{211}$	19.13	19.66	22.16	21.76
$\lg\beta_{210}$	8.85	9.94	13.49	12.56
$\lg\beta_{21-1}$	0.23	0.85	4.64	3.20
pK_a	8.62	9.09	8.85	9.36

Table 6 Stability constants for the ligand L5

	Co(Ⅱ)	Ni(Ⅱ)	Cu(Ⅱ)	Zn(Ⅱ)
$\lg\beta_{210}$	2.17	3.26	8.07	3.12
$\lg\beta_{21-1}$	−7.18	−6.28	−1.72	−6.51
pK_a	9.35	9.54	9.79	9.63

atom of 1,10-phenanthroline and the proton H^+ on nitrogen atom of amino group located near 1,10-phenanthroline are released firstly while another three protons H^+ are still linked to three nitrogen atoms of amino groups of **L4** and the ligand **L4** coordinated with two Cu^{2+} to form the complex $Cu(Ⅱ)_2\mathbf{L4}H_3$. With the increase of the pH value, the protons on three nitrogen atoms of amino groups of **L4** are lost step by step to form $Cu(Ⅱ)_2\mathbf{L4}H_2$ (pH about 3.2), $Cu(Ⅱ)_2\mathbf{L4}H$ (pH about 4.3) and $Cu_2(Ⅱ)\mathbf{L4}$ (pH about 6.5), and when the pH value of titration solution increases to about 7.5 the coordination water on Cu(Ⅱ) losses proton H^+ to form the $Cu(Ⅱ)\mathbf{L4}H_{-1}$. The deprotonation constant of Cu(Ⅱ) **L4** (H_2O) can be obtained according to $pK_a=\lg\beta_{210}-\lg\beta_{21-1}=13.49-4.64=8.85$. These complexes are good nucleophilic metal-bond hydroxide species and they can be as enzyme models for catalyzing the hydrolysis of phosphate esters because of their nucleophilic group OH^-.

3 Conclusions

In this paper, five 1,10-phenanthroline derivatives have been synthesized and characterized. The thermodynamic properties of these ligands and their complexes with transition metal ions Cu(Ⅱ), Ni(Ⅱ), Co(Ⅱ), Zn (Ⅱ) have been studied in aqueous solutions by potentiometric titration. The results show that there is a great difference among the five ligands, we try to explain the difference from many aspects. The results also show that the ligands are of great interest in coordination with metal ions especially transition metal ions Cu(Ⅱ), N(Ⅱ), Co(Ⅱ) and Zn(Ⅱ) which can be used as enzyme models of catalyzing the hydrolysis of phosphate esters[7].

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